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ON THE

PROGRESS OF CHEMISTRY.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1912.

ISSUED BY THE CHEMICAL SOCIETY.

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TRAVEL
IMAGINATION

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Amer. Chem. J.	American Chemical Journal.
Amer. J. Physiol	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Physik	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Arch. expt. Path. Pharm.	Archiv. für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg	Bulletin de l'Academie Impériale des Sciences de St. Pétersbourg.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Föld. Közlöny	Földtani Közlöny.
Gazzetta	Gazzetta chimica italiana.
Gummi-Zeit.	Gummi-Zeitung.
Intern. Sugar J.	International Sugar Journal.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.

* The year is not inserted in references to 1912.

Abbreviated Title.	Journal.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. Phys.	Journal de Chimie physique.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Physikal. Zeitsch.	Physikalische Zeitschrift.
P.	Proceedings of the Chemical Society.
Proc. Amer. Acad.	Proceedings of the American Academy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. London Phys. Soc.	Proceedings of the London Physical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Sienze Fisiche e Matematiche-Napoli.
Rev. Mét.	Revue de Métallurgie.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
T.	Transactions of the Chemical Society.
Tech. Quart.	Technology Quarterly.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Wochensch. f. Brauerei	Wochenschrift für Brauerei.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.

Abbreviated Title.	Journal.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem. . .	Zeitschrift für Elektrochemie.
Zeitsch. Farb. Ind. . .	Zeitschrift für Farbenindustrie.
Zeitsch. Kryst. Min. . .	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem. .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem. .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.

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GENERAL AND PHYSICAL CHEMISTRY.

In accordance with the method adopted in former reports on this branch of Chemistry, no attempt has been made to refer to the whole of the work carried out during the past year. The more important advances in connexion with a limited number of topics are summarised, the results of investigations published in previous years being included when not contained in former reports. Other equally important matters are held over for inclusion in a subsequent report.

The Water–Ice Equilibrium. New Forms of Ice.

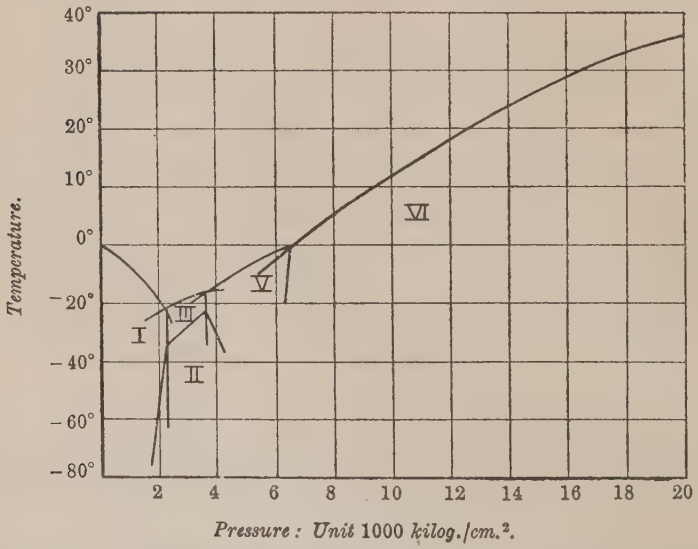
Tammann,[1] in the course of his observations on the behaviour of water under pressure, discovered three new forms of ice, which he designated as Ice II, Ice III, and Ice IV respectively, ordinary ice being Ice I. The highest pressure used by Tammann was 3500 kilog./cm.^{2}. A remarkable advance in this subject has recently been made by Bridgman,[2] who has extended his observations up to a pressure of 20,500 kilog./cm.^{2}. His results in the main agree with those of Tammann at the lower pressures, but he has failed to confirm the existence of Ice IV, and has discovered two new forms, Ice V and Ice VI. There are, therefore, five solid modifications of ice, the regions of stability of which have been established, and possibly one or two other forms which are unstable under all conditions. All of these forms, except ordinary ice, are more dense than water. The effect of high pressures is to remove the abnormalities of water, and there is evidence that the form of ice stable at high pressures is the last form, corresponding with the completely

[1] *Ann. Report*, 1910, 1.

[2] P. W. Bridgman, *Proc. Amer. Acad.*, 1912, **47**, 441 ; *A.*, 1913, ii, 39.

normal liquid. The compressibility of water, both above and below 0°, and of the different forms of ice, has also been determined.

The principle of the method employed in the measurements consisted in plotting the displacement of the piston by which pressure is produced against the pressure. The change of phase, being accompanied by a change of volume at constant pressure, is shown by a discontinuity in the curve of piston displacement against pressure. The pressure at the point of discontinuity gives the equilibrium pressure, and the volume swept out by the piston gives the change in volume on passing from one phase to another. The water was placed in a steel shell, open at the top and completely surrounded by kerosene or gasolene, by which the pressure was trans-



mitted. The pressure was measured by observing the change of resistance of a calibrated manganin wire immersed directly in the same chamber with the water, and was controlled at the lower pressures by a Bourdon gauge. Three different forms of apparatus, which were used according to the temperature range, are described in the original. The success of the investigation appears to have depended largely on the high efficiency of the piston packing, as no leak occurred even at the highest pressures, although in these circumstances a correction had to be applied for the viscous yield of the steel tubes.

The main results of the investigation are shown in the figure; the pressures, expressed in 1000 kilog./cm.² as unit, are plotted as abscissæ against the corresponding temperatures as ordinates. As

usual, each curve represents an equilibrium between two phases, the points where three curves meet—the triple points—equilibrium between three phases. The equilibrium curves were, with one exception, determined with such accuracy that the three curves met naturally at the respective triple points, the exception being the lower end of the V-L curve.[3]

The co-ordinates of the five triple points, the changes of volume ΔV (c.c. per gram), and the latent heats at the same points, are given in the accompanying table. The latent heats ΔH calories per gram were calculated from the observations by means of the equation

$$\Delta H = T\Delta v \,.\, dp/dt,$$

where the symbols have the usual signification. The signs are so chosen that the change of volume is an increase when the reaction runs in the direction in which the symbols read, and similarly the positive sign indicates that heat is absorbed when the reaction proceeds in the direction indicated by the symbols.

Point.	Temperature.	Pressure kilog./cm.^{2}	Change.	ΔV.	ΔH.	Change.	ΔV.	ΔH.	Change.	ΔV.	ΔH.
III-L-I	−22·0°	2115	III-L	0·0466	50·9	L-I	0·1352	−56·1	III-I	0·1818	−5·2
II-III-I	−34·7	2170	II-III	0·0215	12·3	III-I	0·1963	−2·2	II-I	0·2178	10·1
V-III-L	−17·0	3530	V-III	0·0547	0·9	III-L	0·0241	61·4	V-L	0·0788	62·3
V-II-III	−24·3	3510	V-II	0·0401	−16·0	II-III	0·0145	16·9	V-III	0·0546	0·9
VI-V-L	+0·16	6380	VI-V	0 0389	0·2	V-L	0·0527	70·1	VI-L	0·0916	70·3

No evidence was obtained of the formation of Tammann's Ice IV, but as the question of its existence is still open, the symbol Ice IV has been retained for it. In the course of the investigation of Ice VI, indications were obtained of the existence of a sixth form, unstable under all conditions, but the results were not conclusive. Whether there are other forms stable at still higher pressures than 20,000 kilog./cm.^{2} cannot be definitely decided, but as the region of stability of Ice VI is already five times greater than any of the other forms, and the course of the freezing curve and of the change of volume curve is such that both may be extended without difficulty to infinite pressures and temperatures, Ice VI may very well be the final modification.

In consequence of subcooling or superheating it has been found possible to go across nearly every one of the boundary lines into the region of instability on the other side. In accordance with former experience, however, it has been found impossible to superheat a crystalline phase with respect to the liquid.

The Compressibility of Water.

In the course of the investigation the compressibility of water under high pressures has been determined directly[4] at 0° and 22°,

[3] L represents liquid.

[4] *Loc. cit.*, p. 446.

and by a modified method down to about $-20°$. The curves at 0° and 22° obtained by plotting the compressibilities as ordinates against the pressures as abscissæ cross at a pressure of 4000 kilog./cm.^{2}; at low pressures the compressibility at low temperatures is greater than it is at high temperatures, but with rising pressure the abnormality disappears, and beyond 4000 kilog./cm.^{2} the compressibility is higher at the higher temperature. The abnormality at low pressures, followed by normal behaviour at high pressures, is shown still more strikingly by the data below 0°. When volumes per gram as ordinates are plotted against temperatures from $-20°$ to $+10°$ as abscissæ, the curves up to a pressure of 1000 kilog./cm.^{2} show a minimum; at 1500 kilog./cm.^{2} there is both a maximum and a minimum, and at 3000 kilog./cm.^{2} the abnormalities have been entirely smoothed out. The most significant fact in this connexion is that the abnormalities have been completely eliminated without being displaced as regards the temperature at which they occur. The usual explanation of such observations is that water is composed of simple and complex molecules in equilibrium, and that the amount of polymerisation is diminished by rising pressure; but the effect of this would be to displace the region of abnormality from high to low temperatures, which does not occur. A more plausible hypothesis is that the double molecules are much more compressible than the simple molecules, so that the difference in volume between simple and complex molecules rapidly becomes less at higher pressures and polymerisation, even if it exists, will have very little effect on the results. The anomalous decrease of compressibility with rising temperature is presumably due to the fact that at the higher temperatures the double molecules with abnormally high compressibility are becoming fewer. This explanation does not imply that the actual change of size of the molecules under pressure is the chief factor in the change of volume of the substance as a whole—probably the main factor is the closing up of the spaces between the molecules under pressure.

Tammann's theory, which has recently been accepted on mathematical grounds by van Laar,[5] that there is a maximum on the liquid-solid curve of all substances at sufficiently high pressures, is discussed. Although there is some support for the theory in question in the behaviour of the forms of Ice I, III, and V, which are stable at low pressures, the behaviour of Ice VI at very high pressures renders it probable that the liquid-solid curve will continue rising indefinitely as the pressure increases.

The most interesting features found for the equilibrium solid-

[5] *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **11**, 765; **12**, 120, 133; 1910, **13**, 454, 636; *Chem. Weekblad*, 1912, **9**, 744; *A.*, ii, 1040.

solid are the probable passing of the I-II curve through the absolute zero, the enormous increase in reaction velocity on passing a triple point, and the existence in one crystalline form of nuclei about which crystallisation to another form may begin.

The Colour and Constitution of Water.

A long column of water examined by transmitted light is blue at low temperatures, but when the temperature is raised the colour changes to green.[6] The conclusion drawn from these observations that polymerised molecules of water are blue whereas simple molecules are green or yellowish-green, is confirmed by the fact that concentrated solutions of colourless salts, in which the proportion of polymerised molecules must be small, are more green than pure water at the same temperature. Attempts to apply these observations to determine the proportions of simple and polymerised molecules in water by measuring the absorption spectrum, have so far been unsuccessful.

The Specific Heat of Water.

There is still a want of agreement between the results of different observers for the specific heat of water, the value recently found at 80° by W. R. and W. E. Bousfield[7] by a calorimetric method exceeding that obtained by the continuous electric method of Callendar and Barnes[8] by nearly 1 per cent. In order to obtain an independent verification of the specific heat in the neighbourhood of 80°, H. L. Callendar[9] has designed a new method—the continuous-mixture method—according to which a steady current of air-free water at a temperature in the neighbourhood of 100° is passed through an arrangement of concentric tubes, called a heat exchanger, where it loses some of its heat, emerging at a temperature of about 70°. It is then cooled to 30°, and again passed through the heat exchanger as a cold current, abstracting heat from the hot current *by conduction, without actual mixture*, and emerging at a temperature of about 60°. Allowing for the external heat loss, the experiment gives the ratio of the mean specific heat in the interval 70—100° to that in the interval 30—60°. The results of about one hundred and fifty experiments, in which the conditions as to flow and heat loss were varied as widely as possible, were such as to confirm the continuous electrical method over this range of temperature with an accuracy of 1 in 5000.

[6] J. Duclaux and Mme. E. Wollmann, *J. Physique*, 1912, [v], **2**, 263.
[7] *Ann. Report*, 1911, 1.
[8] *Phil. Trans.*, 1902, A, **199**, 55.
[9] *Proc. Roy. Soc.*, 1912, A, **86**, 254 ; *A.*, ii, 428.

The earlier formulæ covering different ranges of temperature from 0° to 100° are now combined into a single formula of a slightly different type:

$$s = 0{\cdot}98536 + 0{\cdot}504/(t + 20°) + 0{\cdot}0084(t/100) + 0{\cdot}0090(t/100)^2.$$

The absolute value of the mechanical equivalent at 20° is 4·180 joules per gram-degree Centigrade; the value at any other temperature is $4{\cdot}180s$.

Theory of Specific Heats. Energy Quanta.

A remarkable theory, which has contributed enormously to our knowledge of specific heats and of molecular mechanics in general, has been developed within the last few years by Planck, Einstein, and Nernst, and its practical applications have been made more particularly by Nernst and his pupils. The new theory, which was introduced by Planck [10] (1906) to explain the phenomena of radiation, and was extended by Einstein [11] to specific heats, is a development of the kinetic theory, and postulates that energy can only be taken up by an atom vibrating about its position of equilibrium in definite increments—the so-called energy quanta. The brief account given here is based mainly on a paper by Nernst.[12]

According to the kinetic theory, molecules are regarded as rigid systems of material points. The mean kinetic energy of a gaseous molecule at the absolute temperature T is made up of the energy of rectilineal motion and of that of rotation. The first is the same for all gases, and is equal to $\frac{1}{2}RT$ in the direction of each of the three axes in space. A single atom is regarded as having no energy of rotation, a molecule containing two atoms can rotate in two planes, and a molecule containing three atoms can rotate in three planes at right angles to each other; for each degree of freedom the energy of the molecule is $\frac{1}{2}RT$. The molecular heats of the three types of gas should therefore be $\frac{3}{2}R$, $\frac{5}{2}R$, and $\frac{6}{2}R$ (2·98, 4·96, and 5·95) respectively, and should be independent of the temperature. The theory is in entire accord with the facts for monatomic gases (up to 2350° the specific heat of argon remains constant at 2·98),[13] but does not hold for polyatomic gases, the molecular heats of which increase with the temperature, and ultimately considerably exceed the theoretical values. This discrepancy could be accounted for if there are other degrees of freedom besides those mentioned

[10] M. Planck, "Vorlesungen über theoretische Physik," 1910; *Ber.*, 1912, **45**, 5; *A.*, ii, 230.

[11] A. Einstein, *Ann. Physik*, 1907, [iv], **22**, 185.

[12] *Zeitsch. Elektrochem.*, 1911, **17**, 265; *A.*, 1911, ii, 464.

[13] M. Pier, *ibid.*, 1909, **15**, 546; 1910, **16**, 897; *A.*, 1909, ii, 789; 1910, ii, 1032.

above; for instance, the vibration of an atom about its position of equilibrium, but as the molecular heats have the theoretical values at relatively low temperatures, and only become larger at high temperatures, it would seem as if new degrees of freedom appear as the temperature rises—a deduction which is inexplicable on the basis of the kinetic theory.

The energy of an atom of a monatomic solid is the sum of the kinetic energy of vibration of the atom about its position of equilibrium, and of potential energy due to the distance of the atom from this position, the two parts being equal. Assuming that the kinetic energy of a solid is the same as that of a gas in temperature equilibrium with it ($\frac{3}{2}RT$), it follows that the total energy of a solid atom should be $3RT$, and its atomic heat $3R = 5{\cdot}955$, which is the law of Dulong and Petit. This deduction of the law is based on the assumption that the force with which an atom is attracted towards its position of equilibrium is proportional to its distance from this position—an assumption which is the more nearly true the smaller the amplitude of the vibration, that is, the lower the temperature. Recent measurements show, however, that at low temperatures many atomic heats are smaller than the above theoretical value,[14] and it is probable that the phenomenon is a general one.

It will now be shown that the deviations in the case of solid substances can be accounted for by the quanta theory, according to which an atom vibrating about its position of equilibrium can only take up energy *discontinuously*, in definite amounts, e, which are directly proportional to the vibration frequency of the atom. In contradiction to the Maxwell law of distribution, according to which the kinetic energy of the atoms of a solid is distributed about a mean value, all values from 0 to infinity being represented, the quanta theory postulates that there are groups of atoms with no kinetic energy, other groups with $2e$, $3e$, etc., and there are no atoms with intermediate quantities of energy. The total energy of the atom of a solid, according to the quanta theory, is $3R\beta\nu/(e^{\beta\nu/T}-1)$, instead of $3RT$, and the atomic heat is:

$$C_\nu = 3Re^{\beta\nu/T}(\beta\nu/T)^2/(e^{\beta\nu/T}-1)^2 \quad . \quad . \quad . \quad . \quad (1),$$

instead of $3R$; ν is the frequency of vibration of the atom, and β a universal constant ($4{\cdot}865 \times 10^{-11}$). The interpretation of the latter formula, and of the modified formula of Nernst and Lindemann,[15] is that the atomic heats of the elements converge to $3R = 5{\cdot}985$, and reach this value at so much higher a temperature the greater the vibration frequency of the atom.

[14] p. 8.

[15] *Zeitsch. Elektrochem.*, 1911, **17**, 817; *A.*, 1911, ii, 1059.

Starting with the assumption that a substance melts when the amplitude of vibration of the atoms about their position of equilibrium is equal to the distance between them, Lindemann [16] has deduced the formula $\nu = 2{\cdot}80.10^{12}\sqrt{T_s/mv^{\frac{2}{3}}}$, where T_s is the melting point, m the atomic weight, and v the atomic volume at the melting point. The values of ν obtained by the latter formula and by formula (1) are in good agreement, especially in the case of the metals, which is a striking confirmation of the validity of formula (1). These formulæ admit of an explanation of the deviations from Dulong and Petit's law. The deviation in the case of carbon is connected with its very high melting point; lithium, with its low melting point, follows the law in spite of its small atomic weight; on the other hand, for lead and mercury, with high atomic weights and low melting points, the values of ν must be small, and these metals should follow the law even at fairly low temperatures, as is found to be the case.[17]

According to the quanta theory, a rise in the temperature of a solid substance at very low temperatures is not attended by an accession of energy, from which it follows that in the neighbourhood of the absolute zero the temperature-coefficients of both the total and free energy approximate to zero, which is Nernst's thermodynamic theorem.

Finally, it is probable that the ordinary laws of mechanics do not apply to atomic vibrations which are enormously more rapid than the terrestrial and astronomical movements on which the laws are based; when the vibration of atoms and molecules about a point is in question (but not in the case of rectilineal motion), the quanta theory must be employed.

In later papers [18] it is shown by experiments carried down to the temperature of boiling hydrogen that the atomic heat falls with diminution of temperature less rapidly than corresponds with Einstein's formula, and the following modification of the latter is proposed:

$$C_v = \tfrac{3}{2}R\{[(\beta\nu/T)^2 e^{\beta\nu/T}/(e^{\beta\nu/T}-1)^2] + [(\beta\nu/2T)^2 e^{\beta\nu/2T}]/(e^{\beta\nu/2T}-1)^2\} \quad (2)$$

which is shown to represent the experimental results, including those given in the accompanying table, with a high degree of accuracy.

Some of the most recent data for atomic and molecular heats down to the boiling point of hydrogen are as follows [19]:

[16] F. A. Lindemann, *Physikal. Zeitsch.*, 1910, **11**, 609; Nernst and Lindemann, *loc. cit.*

[17] F. Pollitzer, *Zeitsch. Elektrochem.*, 1911, **17**, 5; *A.*, 1911, ii, 180.

[18] W. Nernst, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 306; *A.*, 1911, ii, 368; Nernst and Lindemann, *loc. cit.*

[19] *Loc. cit.*

Copper.		Silver.		Lead.		Aluminium.		Potassium chloride.	
T (abs.)	AH.	T (abs.)	AH.	T (abs.)	AH.	T (abs.)	AH.	T (abs.)	$\frac{1}{2}AH$.
88·0	3·38	77·0	4·07	90·2	5·61	88·3	2·62	86·0	4·36
87·0	3·33	53·8	2 90	85·5	5·62	86·0	2·52	70·0	3·79
33·4	0·538	45·5	2·47	38·1	4·45	83·0	2·41	57·6	3·06
27·7	0·324	39·1	1·90	28·3	3·92	35·1	0·33	39·0	1·83
23·5	0·223	35·0	1·58	23·0	2·96	32·4	0·25	26·9	0·76

The atomic heat of the diamond is particularly interesting, as it is zero at some distance above the absolute zero of temperature:

T (abs.)	1169	358	232	209	92	42	30
At. heat	5·45	2·12	0·86	0·66	0·03	0·00	0·00

The specific heats of a large number of oxides, sulphides, and other compounds have been measured at low temperatures[20] in order to determine how far Kopp's law of the additive character of specific heats applies under conditions where Dulong and Petit's law does not apply. In many cases the deviations from the additive law are considerable; this, in terms of the quanta theory, indicates that the vibration frequency of the elements in compounds is different from that of the free elements. In the case of metals such as lead and mercury, which have low vibration frequencies, the observed molecular heats of the oxides and sulphides are in fairly close agreement with the additive law. It has been shown by Koref[21] that the relationship between the vibration frequency, ν, of the free element and that of the element in combination can be put in the form $\nu'/\nu = \sqrt{T'_s/T_s}$, where T_s and T'_s are the melting points of the element and compound respectively.

From the foregoing the remarkable fruitfulness of the quanta theory as applied to solids will be evident, and the consistency of the results obtained in applying it go far towards confirming its validity. It is important to note that the formulæ of Einstein and of Nernst and Lindemann do not contain a single arbitrary constant, as β can be obtained from radiation measurements, and ν can be calculated from the melting point and the atomic volume, as already pointed out. A final test would be to compare the vibration frequencies of the atoms calculated by the above formulæ with those determined directly. This has been done by Koref for the alkali haloids, the vibration frequencies of which have been determined directly by Rubens and Hollnagel,[22] and the agreement is excellent.

Although the problems arising out of the specific heat of solids may now be regarded as to a great extent solved, this is not the

[20] A. S. Russell, *Physikal. Zeitsch.*, 1912, **13**, 59; *A.*, ii, 232.

[21] F. Koref, *ibid.*, 183; *A.*, ii, 328.

[22] H. Rubens and H. Hollnagel, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 26; *A.*, 1910, ii, 172.

case with regard to the more complicated question of the specific heat of gases. Nernst[23] and Bjerrum[24] have deduced formulæ for the variation of the specific heat of gases with temperature on the assumption that besides possessing energy of translation and energy of rotation, the atoms of a polyatomic gas can also vibrate in the direction of the axes joining them. As, however, the formulæ have not yet been fully tested by experiment, this brief reference to the subject must for the present be sufficient.

Nernst's Heat Theorem.

The theoretical basis of Nernst's theorem has been discussed by Planck,[25] more particularly as regards its connexion with classical thermodynamics. The theorem has been adversely criticised from the chemical side in an able paper by Kohnstamm and Ornstein.[26] The authors contend, in the first place, that the heat theorem cannot be deduced from the quanta theory, as stated by Nernst, and quote examples to show that the validity of its application to chemical changes is so far devoid of experimental verification.

On the other hand, a recent investigation which shows the value of the theorem may be cited. The heat of formation of silver iodide calculated from the *E.M.F.* of the silver-iodine cell on the basis of Nernst's theorem[27] gave the value 15,080 calories, whilst the figure given by Thomsen is 13,800 calories. A redetermination of this factor was therefore undertaken, and, as a mean of concordant determinations by three different methods, the value 14,820 calories was obtained, in excellent agreement with the calculated value.

Molecular Weight of Liquids.

Within the last few years doubt has been cast on the applicability of the surface tension method of determining the mean molecular weight of liquids due to Eötvös, and developed by Ramsay and Shields. Walden and Swinne[28] have recently determined the surface tension of thirty-one esters by the capillary tube method, and find that the temperature-coefficients of almost all the liquids examined are greater than 2·12, the normal value of Ramsay and

[23] *Zeitsch. Elektrochem.*, 1911, **17**, 270 ; *A.*, 1911, ii, 464.

[24] N. Bjerrum, *ibid.*, 1911, **17**, 731. Compare Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 743 ; *A.*, ii, 328.

[25] M. Planck, *Ber.*, 1912, **45**, 5 : *A.*, ii, 230.

[26] P. Kohnstamm and L. S. Ornstein, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 802 ; *A.*, ii, 328.

[27] V. Fischer, *Zeitsch. Elektrochem.*, 1912, **18**, 283 ; *A.*, ii, 536.

[28] P. Walden and R. Swinne, *Zeitsch. physikal. Chem.*, 1912, **79**, 700 ; *A.*, ii, 28.

Shields, which would appear to show that they are all dissociated. According to the formula previously deduced, however,[29]

$$Ma_\sigma^2/T_\sigma = 0{\cdot}00435 \log T_\sigma,$$

where Ma_σ^2 is the molecular cohesion at the absolute boiling point, T_σ, and also by the formula of Dutoit and Mojoïu,[30] which gives similar results, the liquids are normal or associated. Similar views as to the inapplicability of the Ramsay-Shields method to liquids of high boiling point have been expressed by other observers. The formulæ of Walden and of Dutoit, so far as tested, appear to give consistent results.

By a thermodynamic method, based on the assumption that the molecular attraction is proportional to the density instead of the square of the density, as assumed by van der Waals, a formula has been deduced[31] which appears to indicate that nearly all the "normal" liquids of Ramsay and Shields are polymerised. This conclusion is not in harmony with much of the recent work on this subject, and would appear to require corroboration.

The conditions which must be fulfilled by an equation which shall admit of a satisfactory calculation of the degree of association of liquids are set out by Tyrer,[32] and the equations hitherto suggested are criticised.

From the results of experiments[32a] on the surface tension of mixtures of alcohol and water by the capillary wave and capillary tube methods, the conclusion is drawn that the latter is subject to certain errors from which the former is nearly free.

Viscosity and Vapour Pressure.

In three papers published almost simultaneously, relationships between the vapour pressure and viscosity of liquids are pointed out. If viscosity is due mainly to attraction between molecules, which attraction has to be overcome when vapour pressure is exerted, it is to be expected that a maximum of viscosity will correspond with a minimum of vapour pressure. This is shown to be the case for a large number of binary mixtures of organic liquids; non-observance of the rule in a few instances is ascribed to chemical combination.[33]

The relationship between viscosity and vapour pressure also holds to some extent for pure liquids. For twenty-two non-associated

[29] *Ann. Report*, 1908, 28.
[30] P. Dutoit and P. Mojoïu, *J. Chim. Phys.*, 1909, **7**, 169; *A.*, 1909, ii, 470.
[31] M. M. Garver, *J. Physical Chem.*, 1912, **16**, 454; *A.*, ii, 830.
[32] D. Tyrer, *Zeitsch. physikal. Chem.*, 1912, **80**, 50; *A.*, ii, 739.
[32a] L. Grunmach, *Ann. Physik*, 1912, [iv], **38**, 1018; *A.*, ii, 903.
[33] O. Faust, *Zeitsch. physikal. Chem.*, 1912, **79**, 97; *A.*, ii, 333.

liquids for which the data are available, the rule holds approximately that the greater the vapour pressure the smaller is the viscosity, but this does not hold for associated liquids.

If any liquid at temperature T has the same viscosity as a standard liquid at temperature T_0, and the ratio T/T_0 is plotted against T, the resulting curve is very nearly a straight line.[34] It is an interesting fact that this relationship holds approximately, even when an associated liquid, such as water, is compared with a non-associated liquid such as mercury. The corresponding relationship for vapour pressures was pointed out long ago by Ramsay and Young. Further, when the logarithm of vapour pressure is plotted against the logarithm of the fluidity, a curve differing very little from a straight line is obtained. A somewhat similar relationship for non-associated liquids has been found by Bingham,[35] who shows that the vapour pressures of such liquids can be calculated if their fluidities and boiling points are known.

In a later paper,[36] the various errors which may affect the results of viscosity measurements are fully discussed, and a new form of viscometer is described, which has been used to determine the viscosity of water between 0° and 100°.

Dissociation and Thermal Conductivity of Gases.

When heat is conveyed between two surfaces at different temperatures through a dissociating gas, the thermal conductivity should be much higher than for a non-dissociating gas, since, in the former case, dissociation is taking place at the hot wall and recombination at the cold wall, and therefore an extra transport of heat due to the heat of dissociation occurs. This reasoning has been applied[37] to settle the question whether any intermediate stages occur in the dissociation $S_8 \rightleftarrows 4S_2$, and also to prove that at high temperatures hydrogen is dissociated into atoms.[38]

The method employed in the latter investigation was to measure the energy required to maintain a tungsten wire at a constant temperature in a gas. In nitrogen and in mercury vapour the rate of loss of energy agrees with the calculated value up to about 3500°; in the case of hydrogen the loss of energy above 2100° becomes greater than the calculated value, and at 3300° is four to five times

[34] A. W. Porter, *Phil. Mag.*, 1912, [vi], **23**, 458; *A.*, ii, 434.

[35] E. C. Bingham, *Amer. Chem. J.*, 1912, **47**, 185; *A.*, ii, 333.

[36] E. C. Bingham and G. F. White, *Zeitsch. physikal. Chem.*, 1912, **80**, 670; *A.*, ii, 1144.

[37] O. J. Stafford and H. von Wartenberg, *ibid.*, 1911, **77**, 66; *A.*, 1911, ii, 700.

[38] I. Langmuir, *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 225; *A.*, ii, 231; *J. Amer. Chem. Soc.*, 1912, **34**, 860; *A.*, ii, 826.

greater. A theory of the conduction of heat in a dissociating gas is given, and the heat of the reaction and the degrees of dissociation at various temperatures are calculated, and shown to be in agreement with van't Hoff's equation connecting the displacement of chemical equilibrium with temperature. Experiments at low pressures show that the phenomenon is a true dissociation, and evidence is adduced to prove that it is not electrolytic.

The calculated heat of dissociation at 3000° for the reaction $2H \longrightarrow H_2$ is about 130,000 cal. at constant volume, or 136,000 cal. at constant pressure.

The Effect of Temperature on the Osmotic Pressure of Sucrose.

During 1911 it was shown by Morse and his colleagues[39] that between 0° and 25° the osmotic pressures of sucrose solutions in all the concentrations examined followed Gay-Lussac's law for gases quite exactly; in other words, between 0° and 25° the osmotic pressure of sucrose solutions is strictly proportional to the absolute temperature. On the other hand, the osmotic pressures exceed the calculated gas pressures by 6 per cent. in 0·2—0·4 weight-normal solutions, and in concentrations greater than 0·4*N* the excess of the former over the latter increases until it reaches 11·5 per cent. in the case of the normal solution. In a recent paper,[40] a complete series of observations at 30°, 40°, 50°, and 60°, and of a number of observations at 70° and 80° are described. The accompanying table contains a summary of the new data with the results at 20° and 25°, taken from a former paper, for comparative purposes.

Weight-normal Concentration.

	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
Ratio of Osmotic to Gas Pressure.										
Temperature.										
20°	1·084	1·062	1·060	1·060	1·067	1 073	1·084	1·093	1·103	1·115
25	1·084	1·059	1·061	1·069	1·065	1·071	1·083	1·093	1·102	1·113
30	1·000	1·020	1·031	1·040	1·050	1·060	1·069	1·081	1·089	1·101
40	1·003	1·011	1·024	1·038	1·046	1·054	1·059	1 067	1 076	1·085
50	1·000	1·002	1·009	1·017	1·025	1·032	1·041	1·049	1·059	1·071
60	1·000	1·001	0·999	1·000	1·006	1·015	1·020	1·027	1·033	1·044
70	—	—	—	—	1·000	1·002	0·999	1·008	1·015	1·023
80	—	—	—	—	—	—	—	1·001	1·000	1·000

The most striking conclusion to be drawn from these numbers is that between 25° and 30° the ratio of osmotic to gas pressure, which

[39] *Ann. Report*, 1911, 9.

[40] H. N. Morse, W. W. Holland, C. N. Myers, G. Cash, and J. B. Zinn, *Amer. Chem. J.*, 1912, **48**, 29; *A.*, ii, 835.

is constant but greater than unity between 0° and 25°, begins to decline in all concentrations, but relatively more rapidly in the more dilute solutions. This diminution in ratio continues as the temperature rises until osmotic pressure becomes, in every instance, equal to the calculated gas pressure of the solute. The further question, as to whether this equality, when once reached, is maintained at all higher temperatures, cannot yet be conclusively stated, but the results for the 0·1 normal solution between 30° and 60° and for the 0·2 normal solution between 50° and 60° appear to show that such is the case.

The figures quoted show that at higher temperatures the solutions follow Gay-Lussac's law only within certain limits. Further, Boyle's law holds quite accurately in some cases, for example, for 0·1, 0·2, 0·3, and 0·4 normal solutions at 60°. In the author's opinion, however, there is no evidence that any of the solutions deviate from Boyle's law; the apparent deviations at low temperatures may be due to some influence—hydration of the solute, for instance—whereby the real concentration becomes greater than the apparent concentration.

It will probably not be possible to carry the measurements much above 80° on account of the destructive action of high temperatures on the membranes.

New Method of Measuring Osmotic Pressures.

A new and interesting method of measuring osmotic pressures has been suggested,[41] based on the following considerations. When a liquid such as ether is in equilibrium with an aqueous solution, the concentration of water in the ethereal layer is less than when water and ether are in equilibrium. If the pressure on the solution in contact with ether is increased, more water passes into the ether, and the pressure required to make the concentration of the water in the ether equal to that observed when pure water is shaken up with ether must presumably be equal to the osmotic pressure of the sugar solution, since the ether–water layer under atmospheric (or any other) pressure and the sugar solution when under a pressure equal to its osmotic pressure are both in equilibrium when brought in contact with pure water (strictly speaking, with water containing a little ether), the former directly, the latter through an ordinary semi-permeable membrane.

Experiments with a solution containing 600 grams of sucrose per litre showed that, interpolating from a curve representing the variation of the concentration of the water in the ethereal layer with pressure, the amount of water taken up from the solution at a

[41] F. T. Trouton, *Proc. Roy. Soc.*, 1912, A, **86**, 149; *A.*, ii, 237.

pressure of 79 atmospheres is equal to that taken up from pure water at a pressure of 1 atmosphere. This value of the osmotic pressure agrees well with that interpolated from the results of direct measurements with a copper ferrocyanide membrane[42] by Lord Berkeley and Hartley (81 atmospheres).

In a letter to *Nature*, Lord Berkeley expresses some doubt as to the theoretical basis of the method; his criticisms have been answered by the author.[42a]

Osmotic Pressure in Concentrated Solutions.

Another interesting contribution to the question as to how far the osmotic pressure in concentrated solutions follows the gas laws may appropriately be considered here. The solubility of carbon dioxide in methyl and ethyl alcohols and in methyl acetate has been determined at $-59°$ and $-78°$ and at pressures from 50 to 700 mm. mercury,[43] and it is shown that even up to 100 atmospheres the osmotic pressures calculated from these observations are in very close agreement with those calculated by the van't Hoff formula on the assumption that the simple gas laws apply. Under corresponding conditions, gaseous carbon dioxide deviates widely from the simple gas laws. A rather complicated formula for the osmotic pressure of concentrated solutions, based on the kinetic theory, is deduced, and shown to be in qualitative agreement with the conclusion which may be drawn from the above observations, that the osmotic pressure of a dissolved substance follows the gas laws much more closely than the gas pressure of the same substance at the same concentration and temperature.

The results are particularly interesting as they admit of a comparison of the osmotic pressure and gas pressure of the same substance under corresponding conditions of temperature and pressure, although it is true that the osmotic pressures are not determined directly, but deduced from the results of solubility measurements.

Osmotic Pressure and Pore Diameter.

The connexion between the size of the pores of a membrane and its capacity to show osmotic effects with a solution of sucrose has been investigated by Bartell.[44] With unglazed porcelain the limit-

[42] *Phil. Trans.*, 1906, A, **206**, 481; *A.*, 1907, ii, 234.

[42a] *Nature*, 1912, **88**, 548; **89**, 32.

[43] O. Sackur and O. Stern, *Zeitsch. Elektrochem.*, 1912, **18**, 641; *A.*, ii, 904; O. Stern, *Zeitsch. physikal. Chem.*, 1912, **81**, 441; *A.*, 1913, ii, 28.

[44] F. E. Bartell, *J. Physical Chem.*, 1911, **15**, 659; **16**, 318; *A.*, 1911, ii, 1072; 1912, ii, 628.

ing value of the pore diameter for the observation of osmotic effects is about 0·4 μ; when scarcely any of the pores exceeded 4 μ, such effects are observed, and are the greater the smaller the pore diameter. The magnitude of the pores was also varied by precipitating various substances in the pores of coarse porcelain. The limiting diameter for osmotic effects in such membranes was rather higher than in fine membranes without a clogging precipitate, and depends to some extent on the nature of the precipitate. The values are, however, of the same order in both cases, and show that pore diameter is one of the main factors in these osmotic phenomena.

The Passivity of Metals.

Few subjects have given rise to so much difference of opinion as the passivity of metals. At least three explanations have from time to time enjoyed considerable favour: (1) the oxide film theory of Faraday; (2) the theory of modifications with different valency[45]; (3) the reaction velocity theory of Le Blanc.[46] The oxide film theory would appear to be difficult, if not impossible, to reconcile with the observation of Hittorf, that chromium can be rendered passive by anodic polarisation in hydriodic acid in the entire absence of oxygen, and also by the failure of optical methods to find any indications of a film on the surface of passive metals[47]; on the other hand, the observation of Müller and Spitzer,[48] that oxygen is evolved at exactly the same potential as platinum anodes coated with iron and iron oxide respectively, appears to be in favour of the oxide theory. The valency theory which is based mainly on the observations of Hittorf, that chromium is bivalent in the active and sexavalent in the passive condition, has not obtained much support in recent years. The view of Le Blanc, which in the first place is little more than a statement of the facts, is that the rate of solution of the passive metal is much less than that of the active metal or, in terms of the osmotic theory, that the solution pressure of the metal is much smaller in the passive than in the active state.

Starting with Le Blanc's conception, Förster[49] and Grave[50] suggest, in entire contradiction to the accepted views, that the passive state is the ordinary condition of iron and nickel, the metals

[45] A. Finkelstein, *Zeitsch. physikal. Chem.*, 1901, **39**, 91; *A.*, 1902, ii, 81.

[46] M. Le Blanc, *Boltzmann Festschrift*, 1904, 183.

[47] W. J. Müller and J. G. Königsberger, *Zeitsch. Elektrochem.*, 1907, **13**, 559; *A.*, 1907, ii, 924.

[48] E. Müller and F. Spitzer, *Zeitsch. anorg. Chem.*, 1906, **50**, 321; *A.*, 1906, ii, 724. Compare also P. Krassa, *Zeitsch. Elektrochem.*, 1909, **15**, 490; *A.*, 1909, ii, 738.

[49] F. Förster, *Abhandlungen der deutschen Bunsengesellschaft*, 1909, No. 2.

[50] E. Grave, *Zeitsch. physikal. Chem.*, 1911, **77**, 513; *A.*, 1911, ii, 896.

only becoming active in the presence of a catalyst. According to Förster, the catalyst is hydrogen, which forms an alloy with the metal; according to Grave it is hydrogen ions. The main evidence in favour of the latter view is as follows: Iron and nickel become active when heated in hydrogen, but become passive when strongly heated in air, nitrogen, or a vacuum. Molecular hydrogen, after being in contact with iron and nickel, does not alter the potential, but ionised hydrogen renders the metals active, and ionised nitrogen renders them passive. Hydrogen ions are given off when a metal changes from the active to the passive state. When iron is saturated with hydrogen ions, the charge given off on heating is greatly increased. When iron is rendered active at one point by bringing it into contact with hydrogen ions, other parts of the metal are rendered active by diffusion.

This explanation of passivity is in accord with the results of an investigation of periodic phenomena at electrodes which can be made passive.[51] In the case of iron the periodic evolution of hydrogen when dilute sulphuric acid is electrolysed at a fixed temperature takes place only at a quite definite potential; if the potential is further increased, the iron becomes passive; at lower potentials it remains completely active. The probable mechanism of the periodic phenomenon is as follows: When the iron is active a considerable current passes, and sufficient oxygen is liberated at the anode to remove all the hydrogen ions, and the electrode becomes passive. The current is therefore much reduced, and as SO_4 ions are always diffusing towards the electrode, sufficient oxygen is not longer liberated to oxidise all the hydrogen ions at the surface of the iron. The latter render the metal active, and this change repeats itself periodically.

In the most recent paper on this subject[52] it is contended that both the formation of a thin film of oxide and the absorption of oxygen[53] as such by the electrode can produce passivity; which of the two factors are mainly concerned depends on the experimental conditions. The oxygen charge is supposed to retard the liberation of cations from the metal, but there does not appear to be any definite evidence of this assumed retardation.

Dunstan and Hill[54] have shown that the passivity and rusting of iron are closely associated, and in this connexion have made an interesting contribution to the subject of passivity. They adduce in favour of the oxide theory the fact that iron is rendered active on

[51] A. Adler, *Zeitsch. physikal. Chem.*, 1912, **80**, 385; *A.*, ii, 891.

[52] G. Grube, *Zeitsch. Elektrochem.*, 1912, **18**, 189; *A.*, ii, 424.

[53] Compare Fredenhagen, *Zeitsch. physikal. Chem.*, 1903, **43**, 1; 1908, **63**, 1; *A.*, 1903, ii, 353; 1908, ii, 679.

[54] W. R. Dunstan and J. R. Hill, *T.*, 1911, **99**, 1853.

heating in hydrogen at 250°, but remains passive on heating in a vacuum at 400°. These results, however, as well as the effect of acids in restoring the activity, can be equally well accounted for on the hydrogen activation theory, and are, in fact, adduced by Grave in support of the latter theory. The hydrogen theory also explains why iron becomes passive in alkalis, a fact which presents difficulties on the oxide film theory. Whether the fact that a sheet of passive iron is rendered active at a point by simple scratching can readily be accounted for on the hydrogen activation theory appears doubtful.

Passivity is not confined to metals of the iron group, as copper, magnesium, zinc,[55] and lead[56] also assume this condition in certain circumstances.

In view of all the facts, it appears improbable that any one cause can be assigned for all forms of passivity. The oxide film theory cannot be regarded as completely disproved by the work of Grave and others, the electrochemical evidence in its favour being in certain cases very strong.

Disappearance of the Electrical Resistance of Metals at very Low Temperatures.

As a result of further very careful measurements on the electrical conductivity of mercury at the boiling point of helium, it appears to be established that the resistance disappears completely at 4·19° abs.[57] The mercury was contained in a series of seven glass U-tubes of about 0·005 sq. mm. cross-section, the tubes being joined together at their upper ends by inverted Y-pieces, which permit of freezing without danger to the tubes, and without breaking the continuity of the threads of mercury. At 4·3° the resistance is 0·0021 of the value for solid mercury at 273° abs.; it falls gradually between 4·3° and 4·21°, but between 4·21° and 4·19° it diminishes very rapidly, and appears to be zero at the latter temperature.

The resistance of platinum also falls very considerably when cooled from the temperature of liquid helium,[58] but appears to be constant between 4·3° and 1·5° abs. This effect is, however, ascribed to impurities in the metal, and it is probable that the resistance of pure platinum would be zero at the temperature of boiling helium.

The fundamental importance of these observations for the theory

[55] Dunstan and Hill, *loc. cit.*

[56] P. P. Lebedeff, *Zeitsch. Elektrochem.*, 1912, **18**, 891 ; *A.*, ii, 1129.

[57] H. Kamerlingh Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 113 ; 1912, **14**, 818 ; *A.*, 1911, ii, 687 ; 1912, ii, 319.

[58] *Ibid.*, 1911, **13**, 1093 ; *A.*, 1911, ii, 487.

of metallic conduction is obvious. According to the author, the disappearance of the resistance of pure metals at a temperature above the absolute zero is to be anticipated according to the quanta theory.[59]

The Mechanism of Electrolytic Conduction.

When a salt solution is electrolysed between electrodes of the corresponding metal, for example, a silver nitrate solution between silver electrodes, it is generally assumed that the change taking place at the anode is the formation of positive ions from the metal. In such a case no polarisation is to be expected at the anode, as the reaction, being ionic, must be extremely rapid, and, as a matter of fact, polarisation has not hitherto been observed in such cells. Recent experiments[60] have, however, thrown an entirely new light on this question. When solid compressed silver salts (the chloride, bromide, iodide, and sulphate were used) are electrolysed between plates of silver and the current then interrupted, considerable polarisation occurs, and this is the greater the lower the temperature. With silver sulphate at room temperature, for instance, an *E.M.F.* of polarisation of 0·312 volt was observed two minutes and 0·125 volt twenty minutes after breaking the circuit. At −80° a polarisation *E.M.F.* of 1·562 volts was observed one minute after breaking the circuit. The results with the silver haloids are similar, but the polarisation is not so great. When the silver anode is replaced by an anode of platinum, the polarisation exceeds one volt, and is not much altered by lowering the temperature from 20° to −80°, whilst the polarisation at a silver anode is greatly increased by lowering the temperature. It is probable, therefore, that the polarisation with silver electrodes takes place only at the anode.

The probable explanation of the above results is that the transport of the current from solid electrolyte to anode is effected by the passage of negative electrons from anions to metal; the discharged anions (presumably free halogen in the case of silver haloids, persulphate ions in the case of silver sulphate) then attack the silver anode, the latter change being greatly retarded by cooling. It is probable that the mechanism is the same in aqueous solution, but in this case the discharged ion in presence of the solvent reacts rapidly with the electrode, so that little or no polarisation occurs.

[59] Compare Nernst, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 306; *A.*, ii, 368.

[60] F. Haber and J. Zawadzki, *Zeitsch. physikal. Chem.*, 1911, **78**, 228; *A.*, 1911, ii, 1053.

Anomalous Molecular Conductivity Curves.

In addition to the anomalous molecular conductivity curves referred to in last year's report,[61] a number of others fall to be considered. The molecular conductivities of sodium, potassium, and lithium acetates in acetic acid on progressive dilution rise to a maximum in approximately normal solution, then fall to a minimum in $N/20$-solution for the last two acetates, in $N/30$-solution for sodium acetate, and beyond these points increase on further dilution.[62] Similarly, the molecular conductivities of methyl, ethyl, and butyl alcohols in liquefied hydrogen chloride decrease with dilution at intermediate concentrations, but show the usual increase with dilution in more dilute solutions.[63]

This subject is discussed by Sachanoff,[64] who divides solvents in which diminution of the molecular conductivity is observed into two classes: (1) those in which all solutes, independently of their nature, exhibit such diminution; (2) those few in which the molecular conductivity as a rule increases with dilution, but with certain dissolved substances diminishes. The behaviour of the amines and certain aliphatic acids in this connexion is as follows, the numbers in brackets representing the dielectric constants. Solutions in liquid ammonia (22 at $-34°$) and methylamine (about 10) show increase of the molecular conductivity with dilution; those in aniline (6·85), ethylamine (6·17), methylaniline (5·93), dimethylaniline (4·48), and amylaniline (4·48) show decrease; those in hydrocyanic (96), formic (57), or thioacetic acid (12·8—17·3) show increase, and those in acetic (6·46) or propionic acid (3·15) diminution. These data show that for solvents with low dielectric constants diminution of the molecular conductivity on dilution is as characteristic a property as increase of the conductivity with dilution with solvents of high dielectric constants. It is suggested that in solvents with low dielectric constants only complexes of solvent and solute can undergo electrolytic dissociation; the gradual decomposition of these compounds on dilution accounts for the diminution of molecular conductivity then observed.

Recent Measurements of Ionic Mobilities.

The question of the mobility of the hydrogen ion in aqueous solution has given rise to a great deal of controversy. The experi-

[61] *Ann. Report*, 1911, 15.

[62] K. Hopfgartner, *Monatsh.*, 1912, **33**, 123; *A.*, ii, 320.

[63] E. H. Archibald, *J. Amer. Chem. Soc.*, 1912, **34**, 584; *A.*, ii, 527.

[64] A. N. Sachanoff, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 526, 534; 1912, **44**, 324; *A.*, 1911, ii, 689, 691; 1912, ii, 422.

mental difficulties in determining it arise mainly from the influence of impurities in the water on the conductivity values in very dilute solutions of acids. As was shown by Drucker,[65] the original number given by Kohlrausch, 353 at 25° (313 at 18°), is certainly too high, and the former observer suggested 346 as a probable value. Noyes and Kato[66] give 348 for very dilute solutions, but state that the value increases considerably with concentration. The assumption of a varying mobility in dilute solution cannot, however, be regarded as proved.[67]

As the accurate determination of Λ_∞ in very dilute solutions of acids offers so serious experimental difficulties, an indirect method, based on the assumption that the true mobility of the hydrogen ion will be that number which gives the most concordant values for the dissociation constant of a weak acid in dilute solution, has been used,[68] apparently with satisfactory results. The mean of the values deduced from a number of experiments with different acids was $H^{\cdot}=347{\cdot}2$ at 25° (or 313·9 at 18°), with a maximum divergence of 0·4.

It is well known that the transport number of the hydrogen ion is not relatively so great in comparison with other ions in solvents other than water as is the case in aqueous solution. In ethyl alcohol at 25° the value, as deduced from measurements with hydrogen chloride, is about 0·65 in fairly concentrated solution, and appears to increase with the dilution.[69] As Λ_∞ for hydrogen chloride in ethyl alcohol is about 66·5, the mobility of the hydrogen ion in ethyl alcohol at 25° is about 43, only one-eighth of that in aqueous solution. The relative velocities of most ions (except when the hydrogen ion is concerned) do not appear to be greatly affected by a change of solvent.

The Ionisation of Strong Electrolytes.

One of the unsolved problems arising out of the ionisation theory is the fact that strong electrolytes do not obey the law of mass action. In this connexion a valuable series of papers by A. A. Noyes and K. G. Falk[70] has recently appeared, in which the most trustworthy data for the freezing-point depression, transport numbers, and electrical conductivity of a large number of salts in

[65] K. Drucker, *Zeitsch. Elektrochem.*, 1907, **13**, 81 ; *A.*, 1907, ii, 225.

[66] A. A. Noyes and Y. Kato, *Zeitsch. physikal. Chem.*, 1908, **62**, 420 ; *A.*, 1908, ii, 346.

[67] R. Wegscheider, *ibid.*, 1909, **69**, 503 ; *A.*, 1909, ii, 965.

[68] J. Kendall, *T.*, 1912, **101**, 1275.

[69] R. T. Hardman and A. Lapworth, *ibid.*, 1911, **99**, 2242 ; 1912, **101**, 2249.

[70] *J. Amer. Chem. Soc.*, 1910, **32**, 1011 ; 1911, **33**, 1436 ; 1912, **34**, 454, 485 ; *A.*, 1910, ii, 929 ; 1911, ii, 861 ; 1912, ii, 526, 527.

aqueous solution are tabulated and critically discussed. The concentrations are expressed in terms of the number of equivalents or of formula weights of salt in 1000 grams of water. The ionisation values are calculated from the cryoscopic data by means of the equation $N = \Delta t / 1{\cdot}858 \,.\, (1 + 0{\cdot}0055\Delta t)$, where Δt is the lowering of freezing point and N is the number of formula weights associated with 1000 grams of water. In the determination of the transport numbers, the electrical conductivity method of Hittorf, the gravimetric method of Lobry de Bruyn, and the moving boundary method of Lodge, Masson, and Steele have been carefully compared The values obtained by the first and last methods agree for uni-univalent salts within the limits of experimental error, but differ by 1—3 per cent. from those obtained by the moving boundary method, and the authors are of opinion that the latter method requires further investigation before trust can be placed in the values obtained by it.

In calculating the degree of ionisation from electrical conductivity measurements, the influence of viscosity on the results is allowed for by using the expression $\alpha = \Lambda\eta / \Lambda_\infty \eta_0$, where η is the viscosity of the solution, η_0 that of pure water, and the other symbols have the usual signification. There are striking similarities in the degree of dissociation of salts of analogous constitution; thus all the chlorides, bromides, and iodides of all the alkali elements have, even up to normal concentration, ionisation values which in scarcely any case differ by more than 1·5 per cent. from the mean, and the nitrates of the alkali elements and potassium chlorate and bromate form another group, for which up to 0·1 normal the ionisation values are practically identical. A consideration of all the results shows, however, that in general ionisation is not an additive property with respect to the ion-constituents; also, that its magnitude is not related to those of the mobilities of the ions. A table of the most trustworthy values for the equivalent conductances of the ions at 18° and 25° is given.

A comparison of the ionisation values derived from cryoscopic and electrical conductivity data calculated as above shows that the values for most uni-univalent substances agree with each other up to 0·1 normal solution within about 2 per cent., but for most uni-bivalent and bi-bivalent salts (especially the haloids of bivalent metals) the agreement is not so good. The deviations for the latter group of salts might be ascribed to the occurrence of intermediate ions (such as $BaCl^{\cdot}$), double molecules [such as $Mg_2(SO_4)_2$], and of complex ions (such as $BaCl_3'$ and $BaCl_4''$), although it is doubtful if a complete explanation is afforded in this way. The fair agreement in the values for uni-univalent salts might be held to confirm

the assumptions on which the methods are based: (1) that the mobility of the ions does not vary with concentration except in so far as the viscosity of the solution varies; (2) that the molal effects of the ions and non-ionised molecules are normal, like those of organic substances. This is evidence, however, that the closeness of the agreement is to some extent illusory, as compensating effects occur, especially in freezing-point determinations, and it is probable that neither of the above principles is strictly accurate.

In connexion with the above paper, McBain [71] contends that the different values afforded for the degree of dissociation of bivalent metal haloids by the cryoscopic and conductivity methods can be fully accounted for on the view that intermediate ions, for example, $BaCl'$, are present in dilute and complex ions, for example, $BaCl_3'$ in concentrated solutions.

The Solubility Product.

Within the last few years, doubt has been thrown on the strict validity of the so-called law of the ionic solubility product, according to which (1) the product of the concentrations of the ions of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone, (2) the concentration of the non-ionised portion of a salt, present as solid phase, has the same value in dilute solutions of other salts as it has when present alone. The law can, of course, only be expected to hold for very dilute solutions, in the presence of a large amount of dissolved substance the solvent medium is no longer the same. In order to test the law, Kendall [72] has determined the solubility of a number of sparingly soluble acids in aqueous solutions of other acids, and shows that the deviations, which may be considerable, are due to the solvent effect of the other acid on the sparingly soluble acid.

A more comprehensive investigation,[73] in which the degrees of ionisation are deduced from the results of electrical conductivity measurements, shows that in many cases the law is not even approximately true. Taking first, as the simplest case, the solubility of uni-univalent salts, the solubility of the non-ionised portion decreases considerably, and the solubility product increases slightly, as the total concentration of the salts and of the ions in the saturated solution increase. There is evidence that the deviation from the theoretical dilution law is due more to abnormal behaviour

[71] J. W. McBain, *J. Amer. Chem. Soc.*, 1912, **34**, 1134 ; *A.*, ii, 893.

[72] J. Kendall, *Proc. Roy. Soc.*, 1911, **A**, **85**, 200 ; *A.*, 1911, ii, 474.

[73] A. A. Noyes and others, *J. Amer. Chem. Soc.*, 1911, **33**, 1643, 1650 ; *A.*, 1911, ii, 1074 ; W. C. Bray, *ibid.*, 1911, **33**, 1673 ; *A.*, 1911, ii, 1075. Compare also W. D. Harkins, *ibid.*, 1911, **33**, 1807, 1827, 1836 ; *A.*, ii, 27, 28.

of the non-ionised substance than to abnormal behaviour of the ions.

In order to investigate the behaviour of uni-bivalent salts, the effect of lead nitrate, potassium oxalate, potassium sulphate, and sodium hydroxide on the solubilities of lead chloride, thallous oxalate, silver sulphate, and calcium hydroxide has been measured, and it is shown that the solubility product increases greatly with increase in the concentration of the bivalent ion added; the large increase in the concentration of the latter ion is not compensated by any great decrease in the concentration of the univalent ion of the salt with which the solution is saturated. In this connexion it must be remembered, however, that the determination of the concentration of the univalent ions is somewhat complicated by the presence of intermediate ions such as $PbCl^{\cdot}$ and $CaOH^{\cdot}$, but the uncertainty arising from this cause is too small to account for the large deviations from the law.

Caesium Nitrate and the Law of Mass Action.

Although the ionic equilibria in aqueous solutions of salts do not in general follow the law of mass action, it has hitherto been accepted, on the basis of the freezing-point determinations of W. Biltz,[74] that cæsium nitrate is exceptional in following the law. This point was of general importance as favouring the view that the deviation of strong electrolytes from the law of mass action is due mainly to hydration of the ions, as other lines of evidence indicate that cæsium nitrate is little, if at all, hydrated in solution. This result appears, however, to be conclusively disproved by the very careful cryoscopic determinations of Roth,[75] who finds that the "dissociation constant" of this salt increases with the concentration in $N/35$- to $N/10$-solution, and only becomes constant at higher concentrations. The validity of the law within certain limits is ascribed to the compensating effect of two factors, namely, hydration, which increases the dissociation constant, and the presence of double molecules, which has the opposite effect.

Catalytic Action of Hydrogen Ions.

Although the investigation of the catalytic action of hydrogen ions has chiefly been carried out with organic compounds, a brief reference to some results of general interest will be in place here.

[74] *Zeitsch. physikal. Chem.*, 1902, **40**, 185; *Zeitsch. Elektrochem.*, 1912, **18**, 49; *A.*, 1902, ii, 310; 1912, ii, 242.

[75] W. A. Roth, *Zeitsch. physikal. Chem.*, 1912, **79**, 599; *A.*, ii, 532. Compare also E. W. Washburn and D. A. MacInnes, *J. Amer. Chem. Soc.*, 1911, **33**, 1686; *A.*, 1911, ii, 1076.

The view has often been expressed, although it never obtained general acceptance, that only the ions are active in chemical changes. One of the results of the important investigations of Goldschmidt on ester formation in alcoholic solution [76] has been the complete disproof of the above assumption, as conclusive evidence has been obtained that in the acceleration of esterification by acids in methyl and ethyl alcohols both hydrogen ions and the non-ionised acid are catalytically active. The main evidence advanced in proof of this statement is that when sufficient of the salt of the catalysing acid is added to reduce the ionisation of the latter practically to zero, the reaction still proceeds at a definite rate, and the assumption that this is due to the non-ionised acid (in other words, to a complex of the non-ionised portion of the acid with the alcohol) is shown to afford a satisfactory explanation of all the facts.

The validity of these conclusions has recently been strikingly confirmed by an investigation [77] of the decomposition of ethyl diazoacetate in the presence of acids according to the equation:

$$CHN_2 \cdot CO_2Et + EtOH = EtO \cdot CH_2 \cdot CO_2Et + N_2.$$

In this case also the reaction proceeds at a definite rate in the presence of a salt of the catalysing acid, and the relationship has been established that the greater the strength of the acid the greater is the catalytic activity, k_m, of the non-ionised portion, as compared with the activity, k_H, of the ionised portion under equivalent conditions. In accordance with this principle, $k_m : k_H$ is 0·0018 for trichloroacetic acid, 0·0012 for trinitrobenzoic acid, and equal to or greater than unity for strong acids, such as hydrochloric and sulphosalicylic. From a comparison of the results in aqueous and alcoholic solutions the ratio $k_m : k_H$ appears to be nearly independent of the nature of the solvent. The well-known fact that the rate of hydrolysis of sucrose increases more rapidly than the concentration of the strong acid (hydrochloric or nitric) used as catalyst can now be accounted for on the assumption that in aqueous solution the catalytic activity of the non-ionised acid is about double that of hydrogen ions in equivalent concentration. Similarly, the accelerating effect of neutral salts may be due to their effect in increasing the concentration of the non-ionised portion of the acid. It would appear that these considerations do not apply to the decomposition of esters by bases, however, as neutral salts have very little influence on the rate of hydrolysis of esters in alkaline solu-

[76] H. Goldschmidt [with O. Udby], *Zeitsch. physikal. Chem.*, 1910, **70**, 627; *A.*, 1910, ii, 283; [with A. Thuesen], *ibid.*, 1912, **81**, 30; *A.*, ii, 1154.

[77] G. Bredig, W. S. Millar, and H. Braune, *Zeitsch. Elektrochem.*, 1912, **18**, 535; *A.*, ii, 748; H. C. H. Snethlage, *ibid.*, 1912, **18**, 539; *A.*, ii, 749.

tion. The matter clearly requires a more detailed investigation, but the results so far obtained are suggestive.

Adsorption Formulae.

The so-called exponential formula, which is generally used to express the results of adsorption measurements, may be written in the form:

$$a = kc^n,$$

where a is the amount of gas or dissolved substance taken up by a definite quantity of adsorbent, c is the concentration of the surrounding gas or that of the solute in the surrounding liquid, and k and n are characteristic constants, n varying in different systems usually between 0·1 and 0·5. According to this formula, the amount of substance adsorbed should increase regularly as the concentration of gas or solution in contact with the adsorbent is increased. Such, however, is not the case. When acetic acid is taken up from aqueous solution by charcoal, a maximum of adsorption is reached in moderate concentration, which is not exceeded when the concentration of the solution is further increased.[78] Further, Arrhenius,[79] on the basis of a critical discussion of the careful measurements on the adsorption of gases by charcoal by Titoff [80] and Miss Homfray,[81] finds evidence of maxima in several instances. The adsorption formula suggested by Arrhenius is of the form:

$$\log_{10} s/(s-x) - 0{\cdot}4343x/s = c/k,$$

where x represents the quantity of substance taken up by 1 gram of charcoal, s the maximum value of x, c the pressure of the surrounding gas or the osmotic pressure of the solute, and k a constant. This formula represents satisfactorily the experimental data of Titoff and of Miss Homfray, above referred to, and also the results of Schmidt on the adsorption of acetic acid by charcoal. This expression has the advantage over the exponential formula that it contains only one arbitrary constant, as the quantity s can be obtained directly by experiment. Schmidt, who was the first to direct attention to the importance of the adsorption maximum, has deduced the alternative formula:

$$[(a-x)s]/v = Kxe^{A(s-x)/s},$$

where x represents amount adsorbed, a the amount of solute

[78] G. C. Schmidt, *Zeitsch. physikal. Chem.*, 1911, **77**, 641; 1912, **78**, 667; *A.*, 1911, ii, 969; 1912, ii, 236. Compare Marc, *ibid.*, 1911, **76**, 58; *A.*, 1911, ii, 258.

[79] S. Arrhenius, *Medd. K. Vetensh. Nobelinst.*, 1912, **2**, No. 7; *A.*, ii, 139.

[80] A. Titoff, *Zeitsch. physikal. Chem.*, 1910, **74**, 641; *A.*, 1910, ii, 1041.

[81] Miss I. F. Homfray, *Proc. Roy. Soc.*, 1910, A, **84**, 99; *Zeitsch. physikal. Chem.*, 1910, **74**, 687; *A.*, 1910, ii, 771, 1041.

originally present, v the volume, s the maximum amount adsorbed, and shows that it represents the experimental results better than the simpler formula of Arrhenius.

A result of considerable importance which has emerged from these investigations is that the adsorption of a gas increases simultaneously with the a term of van der Waals's equation,[82] that is, with the attraction between the molecules, and therefore the underlying cause of adsorption is to be sought in molecular attraction between the molecules of the adsorbed substance and the adsorbent. Such being the case, there should be close analogy between adsorption and compressibility, since the compressibility of a liquid depends on the sum of the external pressure and of the internal pressure, the latter being due to molecular attraction. This view is supported by the fact that the Arrhenius formula represents very accurately the data of Amagat for the compressibility of ether, ethyl alcohol, and carbon disulphide; in this case x represents the density of the liquid, c the total pressure (internal + external), and s the maximum density. "Just as the compressibility is determined by the sum of the external pressure and that due to molecular attraction, so adsorption is determined by the sum of the external gas pressure or osmotic pressure and the attraction pressure between adsorbed molecules and adsorbent" (Arrhenius).

With reference to the view sometimes advanced that adsorption is made up of two parts, a surface action and the formation of a solid solution, Arrhenius is of opinion that the second factor is quite negligible, except for highly penetrating gases, such as hydrogen and helium.

Other Investigations on Adsorption.

A recent investigation by Barger and Miss Field [83] of blue adsorption compounds of iodine has yielded interesting results. The glucoside saponarin has a slight true solubility in water (1 in 7000), and can also be obtained in colloidal solution in much higher concentration. The substance in true solution does not give a blue colour with iodine, but colloidal solutions of the glucoside give the blue colour with iodine in the presence of potassium iodide. These and other results appear to indicate that molecular-dispersed systems are never coloured blue; the blue colour is only obtained with colloids or with other substances when they separate from a solution containing iodine. The conclusion of Küster [84] that the

[82] Titoff, *loc. cit.* ; Arrhenius, *loc. cit.*

[83] G. Barger and Miss E. Field, *T.*, 1912, **101**, 1394.

[84] F. W. Küster, *Zeitsch. physikal. Chem.*, 1895, **16**, 156 ; *A.*, 1895, i, 322.

crystalline blue compound obtained with cholalic acid is an additive compound with iodine in atomic proportions is confirmed, but in the case of the blue, amorphous compounds formed with starch, lanthanum acetate and saponarin adsorption plays a great part.

It has long been known that a solution of iodine in water free from iodide does not colour starch, and the same is now found to be true of cholalic acid and saponarin. The addition of potassium iodide brings about immediate coloration, but in the case of saponarin other electrolytes have the same effect, and although it is impossible to exclude the formation of iodine ions by double decomposition, there is evidence that it is the valency of the cation which is of most importance in this connexion. The influence of electrolytes on the coagulation of the blue hydrosol which saponarin forms with iodine has been investigated in the presence of a very small quantity of potassium iodide. The results show that the saponarin–iodine compound behaves like a typical negative colloid; the average concentrations of uni-, bi-, and ter-valent cations required to produce precipitation are approximately in the ratio 250 : 11 : 1.

Inorganic and organic acids and salts are adsorbed slightly or not at all by starch in an aqueous medium,[85] but alkalis in aqueous solution and hydroxides of heavy metals in aqueous ammoniacal solutions are markedly adsorbed. The results appear to indicate that the adsorption is chemical in nature, consisting of two processes of undetermined character.

The simultaneous adsorption of two substances from aqueous solution by animal charcoal has been examined,[86] solutions of oxalic and succinic acids and of oxalic and benzoic acids being used. Both substances are adsorbed from the mixed solutions to a smaller extent than from the corresponding solutions of the single substances, the mutual influence being such that the diminution of the adsorption of a given substance in the presence of a second substance increases with the extent to which the latter is adsorbed.

Relation between Crystalline and Colloidal States.

A highly important contribution to the relations between the crystalline and colloidal states is furnished by Hardy's study[87] of 5-dimethylaminoanilo-3 : 4-diphenyl*cyclo*pentane-1 : 2-dione. This substance occurs as orange needles or dark red plates. Solutions in ethyl alcohol, ethyl ether, acetaldehyde, acetone, carbon tetrachloride, carbon disulphide, glacial acetic acid, and, doubtfully,

[85] A. W. Rakowski, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 586; *A.*, ii, 743.

[86] H. Freundlich and M. Masius, *Gedenkboek J. M. van Bemmelen*, 1910, 88; *A.*, 1911, ii, 374.

[87] W. B. Hardy, *Proc. Roy. Soc.*, 1912, A, **87**, 29; *A.*, ii, 836.

chloroform and benzene, gelatinise when cooled in a freezing mixture. The presence of water, in which the azomethine is insoluble, does not appear to be essential for gelation, although it accelerates the change by lowering the concentration of the solute. Since the change occurs at least as readily in carbon tetrachloride, a non-associated liquid, as in an associated liquid such as alcohol, the cause of gelation cannot be an intrinsic tendency of the solvent molecule to form complexes among themselves, nor can it be traced to the association of solute molecules with molecules of the solvent if the widely held view be correct that such associations occur only in solvents which are themselves associated.

All the gels liquefy when kept at room temperature with deposition of crystals, so that under these conditions they are labile to the system saturated solution plus crystals. Above a certain temperature gelation does not occur, but crystals are formed directly from the concentrated solution. In the case of 97·5 per cent. alcohol this temperature is about 35°. Between 35° and 5° the gel is labile, whilst below 5° it persists so long as to be sensibly stable.

In the above and in other respects now to be mentioned the process of gelation shows considerable analogy to crystallisation; thus nuclei seem necessary for gelation, as gel formation always starts at distinct points on the wall of the containing vessel. The result is that a fully formed gel, although it appears transparent and homogeneous, has a structure determined by the number and nature of the nuclei; it consists of masses more or less imperfectly joined together, which are of very various sizes in alcohol gels and very uniform in size in carbon tetrachloride gels. The structure can be studied very easily with tetrachloride gels, which are composed of spheres very uniformly 0·14 mm. in diameter, hanging together to form a framework; there is more or less fluid between them. Under the microscope each sphere is seen to be built up of closely packed smaller masses, which are polygonal owing to the close packing, and very uniform in size, an axis measuring 10 μ. The smaller masses are arranged in a pattern which radiates outwards from the centre of the larger sphere. The gels of the azomethine are thus built up of at least two orders of structure.

From the above it appears that the basis of gelation is a formation of vitreous masses, which start from independent centres. Vitrification may involve all the solution or a portion of fluid may persist, in which case two phases result. The phase which separates as spheres on cooling is not always the colloid rich phase.

The probable reason why the azomethine gel slowly liquefies is that between the region of concentration and temperature at which the gel is permanent and the region of simple saturated solution

there is an intermediate region in which the glass melts to a true fluid, which is supersaturated with regard to crystals. In the case of solutions of gelatin or agar-agar this intermediate region does not exist; instead, the glass softens to a viscous fluid, which passes insensibly into colloidal solution. The study of the separation of camphorylphenylthiosemicarbazide from solution in alcohol and toluene has yielded results somewhat similar to those just described.[88] If a 5 per cent. solution in boiling alcohol is slowly cooled, the substance separates in well-formed crystals, but a transparent jelly is obtained if the cooling is sufficiently rapid. The jelly is unstable, and crystals begin to separate after a short time. The observations suggest that the gelatinisation process consists in the separation of the semicarbazide in a highly disperse condition. The network structure, which would appear to be characteristic of the jellies, is considered to be the result of the twinning of the crystal constituents.

The process of gel formation has also been followed by means of the ultramicroscope.[89] The process closely resembles that of the separation of two liquid phases from a solution.[90] In sols containing less than 1 per cent. of gelatin, which do not set on cooling, separate flocculent particles are formed; with increasing concentration the structure becomes less distinct, and finally ultramicroscopically homogeneous owing to the closeness of packing of the jelly elements. No evidence of honeycomb or foam structure has been obtained; such structures described by previous observers were presumably due to refraction effects in the ultramicroscope.

General Theory of Colloidal Solutions.

A general theory of colloidal solutions has been developed by Hardy.[91] It is pointed out that as the state of a colloidal solution is determined, not merely by temperature, pressure, and composition, but also by its previous history, it does not correspond with Gibbs's theory of stability, and therefore the phase rule does not apply to such solutions.

The osmotic pressure in such a heterogeneous system depends on the functions dt/dr and ds/dr, which represent respectively the variation of the surface tension at the composite fluid surface and that of the density of the electric charge at the surface with the radius of the globules of the suspended phase. When this

[88] E. Hatschek, *Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 158; *A.*, ii, 1149.

[89] W. Bachmann, *Zeitsch. anorg. Chem.*, 1911, **73**, 125; *A.*, ii, 145.

[90] Compare W. G. von Lepkowski, *Zeitsch. physikal. Chem.*, 1910, **75**, 608; *A.*, 1911, ii, 95.

[91] W. B. Hardy, *Proc. Roy. Soc.*, 1912, A, **86**, 601; *A.*, ii, 837.

radius exceeds the range of molecular action, the globular suspension represents a phase fully formed, and since the pressure and potentials of the transition layer assume fixed values in these circumstances, dt/dr and ds/dr become equal to zero. The point at which the radius of the globules becomes equal to the range of mutual action of any of the molecules present represents therefore a critical point, and is of great importance in connexion with the theory of colloidal solutions.

The Stability of Oil Emulsions.

The results of an investigation [92] which has thrown considerable light on the question of the stability of colloidal solutions, and therefore has a bearing on the above theory, will now be briefly considered. An oil–water emulsion was prepared, and the difference of potential at the oil–water boundary determined by microscopic observations of the movement of the particles under the influence of a known potential gradient. The influence of electrolytes on the contact potential and on the stability of the emulsion was examined, and it was found that the stability depends almost entirely on the contact potential at the surface of the particles, and scarcely at all on alteration of surface tension; when the contact potential becomes zero the stability of the system is also zero, and coagulation takes place immediately. The concentrations of salts of univalent, bivalent, and tervalent metals required to reduce the charge on the particles to zero are in the same ratio as the minimum concentrations of the same salts necessary to cause immediate coagulation of a colloidal solution.

The above observations, carried out with a typical emulsion colloid, would appear to show that there is no essential difference between the so-called suspension and emulsion colloids, and that the generally accepted system of classifying colloids requires revision.

The Nature of Aqueous Solutions of Soap.

Within the last two or three years a good deal of attention has been devoted to the question of the nature of aqueous solutions of soap. Krafft showed many years ago that soap solutions boil about the same temperature as pure water, from which it would appear that the soap is present in colloidal solution. Later investigations have shown, however, that soap solutions have high electrical conductivity, and they therefore belong to the newly established class of electrolytic colloids,[93] to which Congo-red, casein, and many other

[92] R. Ellis, *Zeitsch. physikal. Chem.*, 1911, **78**, 321 ; 1912, **80**, 597 ; *A.*, ii, 13, 1036.

[93] So termed by Hardy, *Gedenkboek J. M. van Bemmelen*, 1910, 180.

compounds belong, and which are characterised by the fact that they contain both electrolytic and colloidal constituents. As hydrolysis also occurs to a greater or less extent, it is evident that such systems are highly complicated. It may be mentioned incidentally that owing to the difficulty of removing air from the mixtures, no trustworthy conclusions can be drawn from the results of ebullioscopic or vapour pressure measurements on soap solutions.[94]

The curve representing the variation at 90° of the electrical conductivity of sodium palmitate with dilution[95] is remarkable, inasmuch as it shows a pronounced maximum in half-normal solution and a distinct minimum between $N/5$ and $N/10$. No final explanation of these anomalous results can be given until the nature of the equilibria have been fully established. There is evidence that free sodium hydroxide is present, and presumably normal sodium palmitate in true solution and acid sodium palmitate mainly in the colloidal form. The precipitate obtained by salting out sodium palmitate with sodium hydroxide consists mainly of the acid palmitate, with proportions of the normal palmitate depending on the conditions of precipitation. The salting out is not due to a diminution in the ionisation of sodium palmitate by a salt with a common ion, with consequent diminution of solubility, but is an instance of coagulation of a colloid.

The anomalous conductivity curve for sodium palmitate at 90° is closely paralleled by that of the very much more mobile myristate solutions.[96] In the laurate curve, however, both maximum and minimum are obliterated, but only the degree, and not the position of the abnormality in the curves is altered in passing down the homologous series from stearate to laurate.

When electrolytes such as sodium hydroxide and sodium chloride are added in gradually increasing proportion to solutions of sodium palmitate,[97] the viscosity falls at first, reaches a minimum, and then increases rapidly as the electrolyte concentration is further increased. The initial diminution of viscosity may be due to the abstraction of water from the disperse phase, with a consequent diminution in the bulk of the latter; the rapid increase of viscosity above a certain electrolyte concentration is due to the formation of colloidal aggregates, the size of which may increase with increasing concentration of the salt. Results similar to the above, both as regards electrical conductivity and viscosity, have been obtained by

[94] J. W. McBain and Miss M. Taylor, *Zeitsch. physikal. Chem.*, 1911, **76**, 179; *A.*, 1911, i, 349.

[95] McBain and Miss Taylor, *loc. cit.*

[96] J. W. McBain, Miss E. C. V. Cornish, and R. C. Bowden, *T.*, 1912, **101**, 2042.

[97] F. D. Farrow, *ibid.*, 347.

Goldschmidt and Weissmann [98] with solutions of soft soap, and they interpret their results on the lines indicated above. The action of electrolytes with a common ion in dilute solution is to diminish the hydrolysis and degree of dissociation of the alkali salts of the fatty acids, whereas in higher electrolyte concentration the soap is largely present as a hydrophil colloid (similar to gelatin).

Influence of Electrolytes on Electrical Endosmose.

The influence of electrolytes on the amount of electrical endosmose is at present causing considerable interest. Until quite recently our knowledge of the subject was due almost entirely to Perrin,[99] who used diaphragms of various insoluble substances, and compared different electrolytes by finding their influence on the amount of liquid passing through the diaphragm in a given time with a definite potential gradient. The direction of osmosis naturally depends on the sign of the charge on the diaphragm. In pure water most of the diaphragms became negatively charged, as also in very dilute alkaline solution, but acids charge the diaphragm positively, and in the latter case therefore the liquid is transferred towards the anode. Most salt solutions diminish the charge on the diaphragm, and therefore lessen the osmosis.

In a recent investigation by Perrin's method,[1] parchment paper and gels of gelatin (10 per cent.) and agar-agar (1·5 per cent.) were used as diaphragms, and the effect of hydrochloric acid, sodium hydroxide, and certain salts was investigated. With diaphragms of agar-agar and of parchment the liquid was in all cases transferred from anode to cathode; with gelatin diaphragms, on the other hand, the direction of transport was from anode to cathode in the case of solutions of sodium sulphate, sodium nitrate, and potassium hydroxide, but in the reverse direction for solutions of nitric acid and of copper and aluminium nitrates. The effect is greater for tervalent and for bivalent anions than for univalent anions in equivalent concentration, and the amount of liquid transported is still further diminished when bivalent and tervalent cations are present.

Results in substantial agreement with the above were obtained by a different method,[2] a capillary tube partly filled with water or an electrolyte being supported in a horizontal position between two

[98] F. Goldschmidt and L. Weissmann, *Zeitsch. Elektrochem.*, 1912, **18**, 380; *A.*, ii, 728.

[99] J. Perrin, *J. Chim. Phys.*, 1904, **2**, 601; *A.*, 1905, ii, 138.

[1] J. O. W. Barratt and A. B. Harris, *Zeitsch. Elektrochem.*, 1912, **18**, 221; *A.*, ii, 420; *Biochem. J.*, 1912, **6**, 315; *A.*, ii, 729.

[2] G. von Elissafoff, *Zeitsch. physikal. Chem.*, 1912, **79**, 385; *A.*, ii, 419.

discharge points, one of which was connected with one pole of an influence machine, the other earthed. The direction and magnitude of the osmosis can be judged from the movement of the liquid in the capillary when the machine is in action. The marked increase in the effect with the valency of the ion recalls the relative efficiency of the ions in coagulating suspension colloids, and this analogy becomes still more marked from the observation that cations of the heavy metals and of organic bases, which are more active in the coagulation of colloids than corresponds with their valency are also more effective than other bivalent ions in diminishing electro-endosmose. As the former effect can be regarded as mainly conditioned by adsorption, an attempt is made to explain the effects of electrolytes on electro-endosmose as being connected with adsorption.

The subject has also been discussed by Bancroft.[3]

Potentials of the Most Important Standard Electrodes.

A useful summary of the potentials of the most important standard electrodes is given by Auerbach,[4] a member of the German Potential Commission. As zero for electrode potentials should be taken that of the normal hydrogen electrode at the same temperature as the electrode in question, and with a hydrogen partial pressure of 1 atmosphere. The most probable values of ϵ_h are as follows (concentrations in gram formula weights per litre):

Electrode.	e_h in volts at 0°.	18°.	25°.
Hg | Hg_2Cl_2 | KCl 0·1	+0·337	+0·337	+0 337
Hg | Hg_2Cl_2 | KCl 1 0	0·289	0·286	0·285
Hg | Hg_2SO_4 | H_2SO_4 0·1—0·5	—	0·68	—
Hg | HgO | KOH 1·0	0·130	—	0·107
Hg | HgO | NaOH 1·0	0·133	—	0·111
Hg | HgO | NaOH 0·1	0·184	—	0·166

Recent Measurements of E.M.F.

By an indirect method,[5] in which (1) the potential of potassium amalgam was measured against a solution containing a known concentration of potassium ions, (2) the difference of potential between potassium and a potassium amalgam in a solution of potassium iodide dissolved in methylamine was determined, the potential of potassium against a *N*-solution of potassium ions is obtained as −3·2084 volts at 25°, against the normal calomel electrode taken

[3] W. D. Bancroft, *J. Physical Chem.*, 1912, **16**, 312; *A.*, ii, 623.

[4] F. Auerbach, *Zeitsch. Elektrochem.*, 1912, **18**, 13; *A.*, ii, 123.

[5] G. N. Lewis and F. G. Kayes, *J. Amer. Chem. Soc.*, 1912, **34**, 119; *A.*, ii, 225.

as zero. The corresponding value for sodium against *N*-sodium ion is $-2{\cdot}9981$ volts at 25°.

The potential of thallium[6] against a *N*-solution of thallium ion, as measured by means of an electrode of the third kind is 0·4149 volt against the hydrogen electrode as zero.

A careful redetermination of the potential of the chlorine electrode[7] gives for the P.D. $Cl_2 | N\text{-}Cl'$ the value 1·0795 volts against the normal calomel electrode as zero.

The hydrogen and calomel electrodes have been investigated very thoroughly by Loomis and Acree.[8]

A number of papers dealing with *E.M.F.* measurements in solvents other than water have been published during the year. It is known that the Nernst formula giving the relationship between *E.M.F.* and ionic concentration does not always apply to such combinations; an apparent instance of this is the behaviour of hydrogen chloride concentration cells in ethyl alcohol.[9] On the other hand, the Nernst formula holds for solutions of zinc chloride against zinc in alcohol within certain limits of concentration,[10] and also for solutions of silver nitrate against silver in acetone.[11]

The normal potentials of a number of metals in methyl alcohol have been determined with the following results[12]: $Zn \longrightarrow Zn^{\cdot\cdot} = -0{\cdot}6103$; $Cd^{\cdot} \longrightarrow Cd^{\cdot\cdot} = -0{\cdot}40$; $Ni \longrightarrow Ni^{\cdot\cdot} = -0{\cdot}247$ to $+0{\cdot}20$; $Cu \longrightarrow Cu^{\cdot\cdot} = 0{\cdot}320$; $Ag \longrightarrow Ag^{\cdot} = 0{\cdot}807$. As reference electrode a calomel electrode, in which methyl alcohol was used in place of water, was employed; its potential was determined by combining it with an ordinary calomel electrode.

GEORGE SENTER.

[6] J. F. Spencer, *Zeitsch. physikal. Chem.*, 1911, **76**, 360; 1912, **80**, 125; *A.*, ii, 364, 731.

[7] G. N. Lewis and F. F. Rupert, *J. Amer. Chem. Soc.*, 1911, **33**, 299; *A.*, 1911, ii, 364.

[8] N. E. Loomis and S. F. Acree, *Amer. Chem. J.*, 1911, **46**, 585; *A.*, ii, 124.

[9] Hardman and Lapworth, *loc. cit.*

[10] F. H. Getman and V. L. Gibbons, *Amer. Chem. J.*, 1912, **48**, 124; *A.*, ii, 894.

[11] A. Roshdestwensky and W. C. McC. Lewis, *T.*, 1911, **99**, 2138; 1912, **101**, 2094.

[12] N. Isgarischeff, *Zeitsch. Elektrochem.*, 1912, **18**, 586; *A.*, ii, 729.

INORGANIC CHEMISTRY.

Although perhaps the work carried out during the past year does not include any great and far-reaching discovery, yet it may at once be said that a very large number of papers have been published, many of which are of considerable interest and value. A great difficulty must naturally be felt in presenting a report on inorganic chemistry arising from the fundamental importance of many papers which perhaps may be considered more properly as being within the purview of physical chemistry. A few of these which manifestly are of importance in relation to inorganic chemistry have been included.

In the main the report follows in its arrangement the precedent of previous years. A section has been added on the rare earths, and as no especial reference has been made to this branch of work of late, two papers published in 1911 have been included.

Atomic Weights.

During the past year a number of important papers dealing with the determination of atomic weights have appeared.

Nitrogen.—Wourtzel[1] has redetermined the ratio between nitrogen and oxygen, the method involving the determination of the weight of oxygen necessary to convert a known weight of nitric oxide into nitrogen peroxide. Five concordant experiments gave a mean value for the atomic weight of nitrogen as 14·0068.

Potassium and Chlorine.—Reference was made in last year's report to an interesting redetermination of the ratio between potassium and chlorine which was based on a careful analysis of potassium chlorate, very great precautions being taken against contamination of the salt by the chloride. The final series of results gives the atomic weight of potassium as 39·097 and of chlorine as 35·458.[2] These results have been favourably criticised by Guye,[3]

[1] *Compt. rend.*, 1912, **154**, 115 ; *A.*, ii, 248.

[2] Stähler and Meyer, *Zeitsch. anorg. Chem.*, 1911, **71**, 368 ; *A.*, 1911, ii, 881.

[3] *J. Chim. Phys.*, 1912, **10**, 145 ; *A.*, ii, 552.

who concludes that the amount of potassium chloride present in the chlorate was at least sufficiently eliminated to be practically negligible.

Since the Report of the International Committee on Atomic Weights has appeared, two papers have been published dealing with the atomic weight of chlorine. In one of these Wourtzel[4] determines the nitrogen–chlorine ratio by the formation of nitrosyl chloride from nitric oxide and chlorine. As a mean of five results the atomic weight of chlorine was found to be $35{\cdot}460 \pm 0{\cdot}003$ (N = 14·008).

Baume and Perrot[5] also determined the ration of chlorine to nitrogen from the combination of gaseous hydrogen chloride with a known quantity of liquid ammonia, and the value found for chlorine was 35·465 (N = 14·009).

Burt and Whytlaw-Gray[6] have redetermined the density of hydrogen chloride. The gas was absorbed by charcoal, care being taken to remove all mercury vapour by condensation with solid carbon dioxide. The weight of a litre of the gas was found to be $1{\cdot}63915 \pm 0{\cdot}00004$, which is identical with the previously found value. This gives the atomic weight of chlorine as 35·460.

Bromine.—An important paper has appeared by Weber[7] describing his experiments to determine the ratio between hydrogen and bromine. As a mean of ten experiments, Weber found the atomic weight of bromine to be 79·924.

Fluorine.—McAdam and Smith,[8] as a result of experiments on the conversion of sodium chloride into sodium fluoride, have published two preliminary determinations of the atomic weight of fluorine, which are 19·0176 and 19·0133 respectively.

Phosphorus.—Baxter, Moore, and Boylston[9] carried out the analysis of phosphorus tribromide, and found as a mean of three series of experiments the atomic weight of phosphorus to be 31·027 (Ag = 107·88).

Baxter and Moore,[10] from the analysis of phosphorus trichloride, have found, as the mean of their most trustworthy experiments, the atomic weight of phosphorus to be 31·028.

Mercury.—From an analysis of mercuric bromide Easley and Brann[11] have confirmed the atomic weight of mercury as 200·64,

[4] *Compt. rend.*, 1912, **155**, 345 ; *A.*, ii, 934.
[5] *Ibid.*, 461 ; *A.*, ii, 933.
[6] *Trans. Faraday Soc.*, 1911, **7**, 30 ; *A.*, ii, 152.
[7] *J. Amer. Chem. Soc.*, 1912, **34**, 1294 ; *A.*, ii, 1163.
[8] *Ibid.*, 592 ; *A.*, ii, 549.
[9] *Ibid.*, 259 ; *A.*, ii, 347.
[10] *Ibid.*, 1644 ; *A.*, 1913, ii, 43.
[11] *Ibid.*, 137 ; *A.*, ii, 257.

a value agreeing with that previously found by Easley in his work on the chloride.

Tellurium.—As was mentioned in last year's report, Harcourt and Baker have thrown doubt on the work of Flint, in which the latter claimed to have resolved tellurium into two fractions having different atomic weights. Pellini [12] has also come to a similar conclusion. On the other hand, Flint [13] has published a further paper on the subject, in which he points out that the explanation of the lower atomic weight put forward by Harcourt and Baker, namely, the presence of tellurium trioxide, is not sound. Flint gives it as his opinion that the matter has not yet been settled, and promises a further paper on the subject.

Dudley and Jones [14] have carried out spectrographic investigations which are important in the present connexion. They find that there is no variation in the spectrum of the different fractions of tellurium, which indicates that no resolution of tellurium has taken place under the conditions of fractionation. Further work is promised in this direction.

Flint's work has been repeated by W. C. Morgan [15] with larger amounts of material, and although twice as many fractionations were carried out, no evidence of separation was obtained.

Holmium.—Holmberg [16] has carried out determinations on the atomic weight of holmium by means of the sulphate method, and finds, as a mean of six determinations, the atomic weight to be 163·45. In the International Table of Atomic Weights for 1913 this number has been adopted.

Radium.—Two interesting papers on the atomic weight of radium have appeared during the past year. In one, Hönigschmid [17] found from the analysis of a large quantity of radium chloride the atomic weight of radium to be 225·95. In the other, Whytlaw-Gray and Ramsay,[18] by the conversion of small quantities of radium bromide into chloride, found the atomic weight to be 226·36, a result which is in agreement with the well known value of Mme. Curie and of Thorpe.

Palladium.—Shinn [19] has carried out a series of determinations of the atomic weight of palladium, the method used being the reduction of the double chloride of ammonium and palladium by

[12] *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 218; *A.*, ii, 343.
[13] *J. Amer. Chem. Soc.*, 1912, **34**, 1325; *A.*, ii, 1051.
[14] *Ibid.*, 995; *A.*, ii, 935.
[15] *Ibid.*, 1669; *A.*, 1913, ii, 41.
[16] *Arkiv Kem. Min. Geol.*, 1911, **4**, No. 10; *A.*, ii, 163.
[17] *Monatsh.*, 1912, **33**, 253; *A.*, ii, 523.
[18] *Proc. Roy. Soc.*, 1912, A, **86**, 270; *A.*, ii, 413.
[19] *J. Amer. Chem. Soc.*, 1912, **34**, 1448; *A.*, ii, 1178.

formic acid in the presence of ammonia. As a mean of nine determinations the atomic weight was found to be $106{\cdot}709 \pm 0{\cdot}016$.

Uranium.—Lebeau[20] has carried out the reduction of uranyl nitrate dihydrate to uranium oxide by heating the salt in a current of hydrogen at 1100°, and as a mean of five experiments he obtained the value 238·50, thus confirming the previous value obtained.

Iron.—Baxter and Hoover,[21] by the reduction of ferric oxide in hydrogen, find the atomic weight of iron to be 55·847 as a mean of twelve analyses.

Molecular Weights.

Rây, Dhar, and De[22] have determined the vapour density of ammonium nitrite. A weighed quantity of the salt, previously sublimed in a vacuum, is introduced into a Hofmann tube heated to 78° with alcohol vapour. Part of the salt decomposes into nitrogen and water, and part into ammonium nitrate, ammonia, nitric oxide, and water, according to the equation:

$$3NH_4NO_2 = NH_4NO_3 + 2NO + 2NH_3 + H_2O,$$

whilst the remainder exists in the form of undecomposed vapour. The products of decomposition were estimated, and the amount of ammonium nitrite used up in their formation was calculated. This amount deducted from the original quantity gave the amount existing in the form of vapour, and thus, as the volume of the vapour was known, the vapour density could be arrived at. The mean of twenty determinations gave a vapour density of 33·5, the theoretical value being 32·0. The authors point out that the presence or absence of water made little or no difference.

Ramsay[23] has determined the ratio of the specific heats of neon, krypton, and xenon by comparing the wave-length of sound in the gas with that of air. He found the values as follows: Ne = 1·642, Kr = 1·689, Xe = 1·666. These numbers approximate within the limits of experimental error to the theoretical ratio 1·667, and it therefore follows that these three gases, like helium and argon, must be regarded as monatomic. The molecular and atomic weights must be identical.

Preuner and Brockmöller,[24] having devised a spiral manometer made of quartz for the accurate measurement of gas pressures, determined the isothermals of sulphur, selenium, arsenic, and phosphorus, from which they calculated the molecular weight and the

[20] *Compt. rend.*, 1912, **155**, 163; *A.*, ii, 848.
[21] *J. Amer. Chem. Soc.*, 1912, **34**, 1657; *A.*, 1913, ii, 55.
[22] *T.*, 1912, **101**, 1185.
[23] *Proc. Roy. Soc.*, 1912, A, **86**, 100; *A.*, ii, 251.
[24] *Zeitsch. physikal. Chem.*, 1912, **81**, 129; *A.*, ii, 1145.

dissociation of the vapours of these substances. They determined the isothermals of selenium at 550°, 600°, 650°, 700°, 750°, and 800°, and found that the equilibrium $Se_6 \rightleftarrows 3Se_2$ takes place over this region. At low and high temperatures there is some evidence of Se_8 and Se atoms respectively. In the case of sulphur vapour, S_8, S_6, S_2, and S are present in amounts depending on the conditions of temperature and pressure. The isothermals of phosphorus and arsenic were measured at 800°, 900°, 1000°, 1100°, and 1200°, and from these curves the authors find that tetra-atomic and diatomic molecules as well as single atoms are present.

The density of phosphorus vapour has been determined with great accuracy by Stock, Gibson, and Stamm [25] with Gibson's membrane manometer.[26] The investigations extended over a temperature range of 500° to 1200°, and the first conclusion arrived at is that phosphorus vapour obeys Boyle's and Gay-Lussac's laws between 500° and 700° and 240 and 300 mm. pressure, and that it consists entirely of P_4 molecules. At higher temperatures dissociation into P_2 sets in, especially at lower pressures. The maximum degree of dissociation observed (two-thirds of the P_4 having dissociated) was at 1200°, and at a pressure of 175 mm. The authors prove that the only equilibrium concerned is $P_4 \rightleftarrows 2P_2$. They also calculated that at the temperature of 1300° the amount of dissociation would be 60 per cent. at 760 mm. and 89 per cent. at 100 mm. pressure.

These results differ from those of Preuner and Brockmöller mentioned above, and the authors criticise those results which would seem to point to there being some phosphorus atoms present at the higher temperatures. They point out that whereas they used carefully purified red phosphorus, Preuner and Brockmöller used commercial yellow phosphorus, which they merely washed several times.

Valency.

Some interesting experiments have been carried out by Ephraim [27] on the hexammine compounds of certain metals, with the view of obtaining a quantitative measurement of the auxiliary valencies in these compounds. Ephraim points out that as these compounds are formed by virtue of the secondary valencies of the principal metallic atom in the molecule it should be possible to determine the relative strength of these auxiliary valencies by measuring the dissociation pressure of the hexammine compounds. The author

[25] *Ber.*, 1912, **45**, 3527; *A.*, 1913, ii, 43.
[26] To be described later.
[27] *Ber.*, 1912, **45**, 1322; *A.*, ii, 546.

considers that if the pressure is kept constant the temperature at which the decomposition occurs will be a measure of the energy of the auxiliary valencies because the decomposition of the molecular complexes must be dependent on three factors, namely, the pressure, temperature, and affinities of the constituents.

In one series of experiments he finds that the temperature at which the dissociation pressure of the hexammine chlorides of glucinum, nickel, cobalt, iron, copper, manganese, zinc, cadmium, and magnesium is equal to 500 mm. decreases as the atomic volume of the metal increases. In other words, the auxiliary valency of the metal is a function of its atomic volume. As Ephraim points out, the atomic volume is not the only factor, because copper and iron, which have the same atomic volume, have not the same affinity towards ammonia. The dissociation pressures of the hexammine compounds of these two metals are similar, but not identical. The stability of the hexammine compounds also decreases with increase of atomic volume, and it is an interesting fact that no single metal with an atomic volume greater than 14 can form a hexammine derivative which is stable at the ordinary temperature. Similarly, in the case of glucinum, the atomic volume of which is 5·26, the hexammine derivative is so stable that it decomposes in other ways before the temperature is sufficient to give an ammonia pressure of 500 mm.

He also finds that the influence of the atomic volume is less the larger its value, for of seven hexammine chlorides examined it was found that the value of $\sqrt[3]{T}$. $\sqrt[3]{v}$ was approximately constant, where T is the absolute temperature at which the ammonia pressure is equal to 500 mm., and v is the atomic volume.

It was also found that the acid radicle has some influence on the energy of the auxiliary valencies; for example, the ratio of the absolute temperatures at which the dissociation pressures of nickel chloride and nickel bromide is equal to 500 mm. was 1·073, and in the case of the chloride and bromide of cadmium this ratio was 1·086. This factor Ephraim calls the tension-modulus, and taking 1·08 as the mean of the above two values he calculates the dissociation pressure of the hexammine bromide of cadmium from the experimentally found value for the chloride. The value obtained is 349·3, whilst the experimental value is 347·5, which is quite within the limits of experimental error. In exactly the same way the values of the tension-moduli Br/I, Cl/I, SO_4/I were measured and found to be constant. The only exceptions were the hexammine compounds of zinc. The constant ratio between the tension-moduli was also found to hold good over considerable ranges of pressure; for example, the ratio for the bromide and iodide of cadmium

between the pressures of 103 and 780 mm. was found to have a mean value of 1·066.

This therefore appears to be a special case of Ramsay and Young's rule, and it was also found that this rule could be applied to the hexammine compounds of all the metals examined between the limits of 200 and 700 mm. pressure. From the dissociation-pressure curves the heat of formation, Q, was calculated from the expression:

$$Q = \frac{T_1 \cdot T_2}{T_1 - T_2} \cdot \log \frac{p_2}{p_1}.$$

From the values obtained it follows that for equal dissociation pressures Q/T is very nearly constant, which corresponds with Trouton's law. This was previously shown by Matignon.[28]

The value of the constant Q/T for dissociation pressures of 500 mm. was found to be between 0·030 and 0·036.

In connexion with this it is interesting to note that Chauvenet[29] found for $ThCl_4,18NH_3$ the value of Q/T to be 0·032.

Allotropy.

Stock, Schrader, and Stamm[30] have carried out an investigation on the transformation of yellow phosphorus into red phosphorus photochemically. The yellow phosphorus was placed in a side-tube in an exhausted flask. By local cooling a thin layer of yellow phosphorus was obtained on the walls of the flask, and this film was illuminated on the inner side by rays from a mercury lamp. The residual yellow phosphorus was removed by cooling the side-tube with liquid air for several days. It was found that the violet end of the spectrum was most active in the conversion, and that temperature had very little influence. The density of the red phosphorus thus obtained varied from 1·95 to 2·25, the darkest in colour being the heaviest. It is possible that some crystals were present. It was also found that rapid cooling of phosphorus vapour gives red phosphorus, the amount obtained increasing with the temperature to which the vapour was heated before being suddenly cooled. The authors conclude that the two varieties of phosphorus are chemically different, and that the red variety is formed by the union of dissociated phosphorus particles with one another or with undissociated phosphorus molecules. Red phosphorus prepared in this way is yellowish-red to blood-red in thin layers, and black with a violet glance in compact pieces. When ground to a powder it resembles the commercial article. Its maximum density was 2·215, and it appears to be crystalline. It is stable in air, is only

[28] *Compt. rend.*, 1899, **128**, 103; *A.*, 1899, ii, 273.
[29] *Ann. Chim. Phys.*, 1911, [viii], **23**, 275; *A.*, 1911, ii, 586.
[30] *Ber.*, 1912, **45**, 1514; *A.*, ii, 639.

slowly attacked by boiling sodium hydroxide, and does not give a red solution in alcoholic potassium hydroxide solution.

Hesehus [31] has studied the properties of diamond, graphite, and charcoal, and he shows that the differences between the contact electrification of the allotropic modifications depend, not only on their surface density, but also on the capacity of the atoms for ionic dissociation. It would seem from this result of Hesehus that in all probability the catalytic action of the various allotropic modifications would depend on the residual affinity.

Combustion.

Rhead and Wheeler have published papers in which they deal with the equilibrium between carbon dioxide and carbon, and the oxidation of carbon itself. In the first paper [32] they describe their investigations into the rate of reduction of carbon dioxide by carbon at various temperatures. The method consisted in the circulation for known periods of carbon dioxide over carbon heated to different temperatures, the time taken for a complete circulation of the gas through the apparatus having been previously determined. The amount of reduction of the carbon dioxide was obtained from the increase of pressure in the apparatus. The results show that there is a considerable falling off in the amount of reduction taking place in a given time when the temperature falls below 1000°. One set of experiments was carried out with a mixture containing 80 per cent. of nitrogen and 20 per cent. of carbon dioxide, and this has some interest from the point of view of producer gas, because they found that owing to the short time of contact in the producer a temperature of more than 1100° is necessary for the maximum production of carbon monoxide. The presence of the 80 per cent. of nitrogen causes a general retardation in the rate of reduction, and so enabled the authors to appreciate the true relative rates at the higher temperatures. In the second paper [33] they consider the oxidation of the carbon itself. In connexion with the oxidation of carbon considerable evidence has been advanced, both in favour of the oxidation to carbon monoxide and in favour of the oxidation to carbon dioxide. It is perhaps more generally accepted that the reaction takes place in the following way:

$$(a)\ C + O_2 = CO_2; \qquad (b)\ CO_2 + C = 2CO.$$

The work of Dixon and also that of H. B. Baker would seem to favour the view that the carbon is oxidised first to carbon monoxide, as expressed by:

$$(c)\ 2C + O_2 = 2CO,$$

[31] *J. Russ. Phys. Chem. Soc.*, 1911, **43**, *Phys. Part*, 365; *A.*, ii, 121.
[32] *T.*, 1912, **101**, 831. [33] *Ibid.*, 846.

and that any carbon dioxide is due to the process:

$$(d)\ 2CO + O_2 = 2CO_2.$$

Rhead and Wheeler point out that if the relative rates of (*a*) and (*c*) could be determined under conditions when the amounts of (*b*) and (*d*) are inappreciable, the matter would be solved. They find, however, that during the oxidation of the carbon at low temperatures neither (*a*) nor (*c*) takes place exclusively, and they are obliged to conclude that both carbon monoxide and carbon dioxide are simultaneously produced by the direct oxidation of carbon.

Wieland[34] deals with the reaction between carbon dioxide and water in the presence of palladium-black. He finds that the first product is formic acid, which then gives carbon dioxide and hydrogen, the hydrogen being retained by the palladium. The intermediate existence of formic acid was proved by chemical means Wieland also showed that formic acid is an intermediate product in the hot combustion process. If a carbon monoxide flame is allowed to play on ice, the presence of formic acid in the melted ice can readily be proved. The combustion of the hydrogen from the formic acid gives the water which is necessary for the combustion to proceed, and prevents the reversible reaction from taking place. Traube's view of hydrogen peroxide playing an important part is wrong, for the hydrogen peroxide only occurs as a subsidiary product in the first stage of the combustion of the hydrogen from the formic acid. It is well known that the platinum metals catalyse the reaction:

$$H{\cdot}CO_2H = H_2 + CO_2,$$

and in the case of palladium the catalytic influence is so great that the evolution of hydrogen is stronger than the absorption of hydrogen by the palladium, with the result that hydrogen is evolved. If the palladium-black has previously been ignited, its power as a catalyst is destroyed.

F. Meyer[35] describes experiments to show that the outer zone of a reversed flame is strongly reducing, so that any substance made to pass through the flame from the inside to the outside will be reduced, and remain reduced. It is necessary that the combustion products of the flame should be equal to one of the products formed by the reduction of the substance, for example, a chlorine–hydrogen flame must be used for the reduction of chlorides, the chlorine flame burning in a quartz jet inside hydrogen. Meyer found that this reduces stannic chloride to stannous chloride, arsenic chloride to arsenious chloride, and titanium tetrachloride to titanium trichloride.

[34] *Ber.*, 1912, **45**, 679; *A.*, ii, 347.
[35] *Ibid.*, 2548; *A.*, ii, 1051.

Sulphuric Acid Manufacture.

Reynolds and Taylor[36] have carried out a series of experiments with the view of testing the theory put forward by Raschig[37] of the chamber sulphuric acid process. Raschig supposes that an unstable nitrososulphonic acid is first formed by the action of sulphur dioxide on nitrous acid, as shown by the equation:

$$HNO_2 + SO_2 = ONSO_3H,$$

and that this acid is at once transformed by more nitrous acid into another unstable compound, nitrosisulphonic acid:

$$ONSO_3H + HNO_2 = H_2NSO_5 + NO,$$

and that this new acid then decomposes into sulphuric acid and nitric oxide:

$$H_2NSO_5 = H_2SO_4 + NO.$$

Raschig states that his nitrosisulphonic acid is identical with the violet acid discovered by Sabatier.

This theory was somewhat modified by Divers,[38] who points out that Raschig's nitrososulphonic acid has probably no existence, and that the evidence is all against the existence of nitrosisulphonic acid. Reynolds and Taylor confirm the conclusion of Divers that nitrososulphonic acid has no existence, and prove by experiment that dilute solutions of nitrous and sulphurous acids mutually decompose one another with evolution of nitrous oxide. They also confirm Divers' conclusion that this reaction takes place in two stages:

(i) $HNO_2 + 2H_2SO_3 = H_2O + HON(SO_3H)_2.$

(ii) $HON(SO_3H)_2 + HNO_2 = 2H_2SO_4 + N_2O.$

According to Raschig, the nitrososulphonic acid being formed in a strong acid solution containing excess of sulphurous acid at once undergoes decomposition according to the second equation above. In his experiments potassium iodide was added to the solution to indicate whether excess of nitrous acid was present or not. Reynolds and Taylor prove that the evolution of nitric oxide in the experiment described by Raschig in support of his second equation is due to the action of nitrous acid on hydriodic acid. Raschig attached great importance to the violet acid discovered by Sabatier. He gives experiments to prove that although this compound is produced in the reduction by mercury of a solution of chamber crystals in 85 to 100 per cent. acid, it was not formed in more dilute acid in this way, and he concluded that the chamber crystals could not exist in acid containing less than 80 per cent. of sulphuric

[36] *J. Soc. Chem. Ind.*, 1912, **31**, 367; *A.*, ii, 550.

[37] *Ibid.*, 1911, **30**, 166; *A.*, 1911, ii, 272.

[38] *Ibid.*, 594; *A.*, 1911, ii, 596.

acid. Hence, as he found that the violet acid can be formed by the action of sulphur dioxide on nitrous acid in a 70 per cent. solution of sulphuric acid, he maintains that the violet acid is the direct product of the interaction between nitrous and sulphurous acids, and that it could not have been formed by the reduction by sulphurous acid and chamber crystals, because the latter were non-existent.

Reynolds and Taylor prove conclusively that chamber crystals can exist even in 60 per cent. sulphuric acid, and they satisfy themselves that Raschig's explanation of the formation of sulphuric acid is wrong. Their evidence proves first that the only gaseous product in the interaction of sulphurous and nitrous acids is nitrous oxide, and secondly, that Sabatier's violet acid is only formed in solutions containing chamber crystals; thus they conclusively indicate the futility of all attempts to account for the formation of the bulk of the sulphuric acid in the chambers by the intermediary formation of nitrogen sulphonic acids. They believe that the old views substantially represent the course of the process, namely:

(i) $SO_2 + H_2O = H_2SO_3$.
(ii) $H_2SO_3 + NO_2 = NO + H_2SO_4$.
(iii) $2NO + O_2 = 2NO_2$.

The nitrous oxide which escapes may be a measure to some extent of the extent to which nitrogen sulphonic acids are formed, although the work of Moser [39] leaves it uncertain as to whether this may not have been partly derived from the decomposition of the nitric oxide in contact with the water locally. It must be regarded as doubtful if nitrososulphuric acid (chamber crystals) plays an important part in the process. The authors agree with Divers in expressing a doubt as to whether it is ever formed except by the action of sulphuric acid on one of the oxides of nitrogen, but as sulphurous acid reacts with a solution of chamber crystals some sulphuric acid is possibly formed in this way.[40]

In connexion with the contact process of sulphuric acid manufacture, Wieland [41] has investigated the reaction which takes place when moist sulphur dioxide is passed over palladium-black, oxygen being rigidly excluded. He found that considerable heat is developed, and that after driving off the excess of sulphur dioxide with carbon dioxide and extracting the palladium-black with water, considerable quantities of sulphuric acid are present in the solution. This sulphuric acid is formed according to the equations:

$$H_2SO_3 = SO_3 + H_2 \text{ and } SO_3 + H_2O = H_2SO_4.$$

[39] *Zeitsch. anal. Chem.*, 1911, **50**, 401; *A.*, 1911, ii, 598.

[40] For further experiments contradicting Raschig's theories see Manchot, *Zeitsch. angew. Chem.*, 1912, **25**, 1055; *A.*, ii, 637.

[41] *Ber.*, 1912, **45**, 685; *A.*, ii, 343.

It was not found possible to detect the hydrogen which is produced according to the first equation, for sulphur is deposited in its place, being formed by the action of palladium hydride on sulphur dioxide. The reaction took place according to the equation:

$$SO_2 + 2H_2 = 2H_2O + S,$$

this being shown by the sulphur which is produced when a solution of sulphurous acid is shaken with palladium hydride. Further, if a palladium-black is used which has initially been freed from hydrogen, the yield of sulphuric acid is increased and less sulphur is formed, which suggests that in the contact process for making sulphuric acid the above equations represent what really happens, the hydrogen formed in the first reaction being oxidised to water by the oxygen which is mixed with the sulphur dioxide. Wieland points out that this view is supported by the fact that no union takes place between the sulphur dioxide and the oxygen if these gases are dry.

The Rusting of Iron.

An important contribution to the literature on the rusting of iron has been made by Lambert.[42] In spite of the fact that much experimental work has been done in recent years to prove that ordinary iron will always undergo corrosion when placed in contact with water and oxygen, even in the absence of carbon dioxide and other acids, this work has been criticised by the supporters of the acid theory on the ground that sufficient care has not been taken to remove all traces of carbon dioxide from the apparatus. In the present paper Lambert describes his experiments, in which iron was exposed to pure water and oxygen, the most rigid precautions being taken to exclude every trace of carbon dioxide and any other acid. Both the oxygen and the water were subjected to a very careful spectroscopic test, and not the slightest trace of carbon dioxide was found in either. The result of the experiments was that the rusting seemed to take place as quickly as in ordinary air. It can no longer be maintained that carbon dioxide or any other acid is the dominant factor in the atmospheric corrosion of commercial iron. As was pointed out in last year's report, an electrical theory has been put forward to explain this phenomenon, and Lambert develops this theory in his paper, and brings forward considerable evidence in strong support of it. In the first place, some absolutely pure iron was prepared, and it was found that no trace of corrosion took place when it was kept in contact with either pure water and pure oxygen, or air and ordinary tap water, for an apparently indefinite time. The explanation of this fact is

[42] *T.*, 1912, **101**, 2056.

to be sought in the greater homogeneity of the iron. If the iron be really homogeneous, and all parts have the same solution pressure, then sufficient difference of potential will not exist, and no rusting will take place. Furthermore, some pieces of this pure iron which have been exposed to water and air for some months without showing any corrosion were carefully dried; some of the pieces were then placed in an agate mortar and pressed strongly with an agate pestle, whilst others were left untouched. All were then put in contact with the water and exposed to the air. Those pieces which had been pressed rapidly corroded, rust forming on those parts of the iron which had not been pressed, whilst the parts which had been in actual contact with the polished agate remained quite bright. Those pieces of iron which had not been subjected to pressure showed no sign of corrosion. Evidently, therefore, the application of the pressure induced a change in the iron, giving it a new solution pressure, so that electrical action was set up when it was placed in contact with water. An interesting fact was also noticed in that chemically pure iron can be exposed for an apparently indefinite time to a saturated solution of copper sulphate or copper nitrate without the slightest trace of copper being deposited. Copper is, however, deposited on the iron if it is pressed in an agate mortar before being put in the solution, or if pressed with a quartz rod whilst under the solution. In the case of copper chloride, however, even the purest iron reacts, and becomes coated with copper immediately it is put into the solution. The author has no completely satisfactory answer to the question as to why the chloride has this abnormal effect, and for the present leaves it an open question. It is interesting to note that all the samples of pure iron may not behave exactly in the same way, even though prepared from the same specimen of ferric nitrate. Some will show no corrosion after contact with water in air for an indefinite time, whilst other specimens show corrosion in a few hours. The difference in behaviour cannot be due to different chemical composition, and must be due to physical differences produced by variation in tempering and rate of cooling in the preparation. It would seem probable from these results that the fundamental cause of the corrosion of iron is not carbon dioxide or any other acid, but that the cause is rather to be sought in the difference of solution pressure of the different parts of the iron, differences which may persist even in the most highly purified form of the metal.

Electric Discharge.

During the past year Strutt has carried out further experiments on his active modification of nitrogen. He finds[43] that the active

[43] *Proc. Roy. Soc.*, 1912, A, **86**, 262; *A.*, ii, 447.

modification emits its energy more quickly and reverts sooner to ordinary nitrogen if it is cooled. This would appear to be the first case in which a chemical or physico-chemical change is increased in velocity by cooling. If the glowing gas is compressed to a small volume it flashes out with great brilliance, and exhausts itself in so doing. The glow transformation seems to be a multimolecular phenomenon. The active nitrogen may revert to ordinary nitrogen in two ways. The first way consists in a volume change accompanied by a glow, and the second in a surface action on the walls without glow. This is analogous to hydrogen and oxygen producing water, which may be a surface or a volume effect according to the circumstances. In a second paper Strutt[44] describes experiments which prove that active nitrogen is highly endothermic, but that its energy is of the same order as that of other chemical substances. In the reversion to ordinary nitrogen, the number of atoms ionised is a very small fraction of the total concerned. The ionisation, therefore, is a subordinate effect, and may be due to light of very short wave-length being emitted during the change. In this paper further proof is adduced that the change is accelerated by cooling, and Strutt puts forward the view that the phenomenon is connected with a monatomic condition of the nitrogen molecule. Strutt and Fowler[45] describe the production of various spectra by means of the nitrogen glow, and they do not find that those spectra differ materially from those produced in ordinary ways. Certain minor differences are, however, to be noticed, and the method certainly adds to our resources in producing spectra.

In this connexion an interesting paper has been published by Lowry[46] dealing with the action of the spark gap and an ozonising apparatus on the production of nitrogen peroxide. The presence of this gas was detected, and its amount estimated spectroscopically. A 19·5 m. [64 feet] column of the gas was used, and the light of a Nernst lamp, after passage through this, was examined with a single-prism spectroscope, and also its spectrum photographed. The ozoniser consisted of 13 Andreoli aluminium grids, 76·2 × 76·2 cm. [30 × 30 inches], separated by micanite. In the spark gap apparatus there were in the first experiments three spark gaps made by fixing iron studs 0·238 cm. [3/32nd inch] apart. It was found that if a stream of air was passed through the ozoniser or through the spark gaps alone, no trace of nitrogen peroxide was visible, but if the air was passed through the spark gaps and ozoniser arranged in series, then about 1/4000th part by volume of nitrogen peroxide was produced. It was also noticed that if a current of air passed

[44] *Proc. Roy. Soc.*, 1912, A, **87**, 179; *A.*, ii, 935.
[45] *Ibid.*, 1912, A, **86**, 105; *A.*, ii, 214.
[46] *T.*, 1912, **101**, 1152.

through the spark gaps first and then through the ozoniser, about an equal quantity of nitrogen peroxide was obtained. This result is somewhat extraordinary, seeing that ready-made nitrogen peroxide is bleached on being passed through an ozoniser. Lowry also found that if the ozoniser and spark gap were used in parallel and the air emerging from them was mixed, nitrogen peroxide was also produced. Evidently, therefore, the nitrogen peroxide cannot be due to a simple electrical action, but must be the result of a chemical interaction between ozone and some oxidisable form of nitrogen produced in the spark gap. A second spark gap apparatus was set up containing seventeen spark gaps, and the whole of the available electrical energy was concentrated on this. When the air issuing from this apparatus was rapidly passed through the absorption tube it showed the presence of 1/7000th part of nitrogen peroxide, and when passed more slowly it showed 1/3000th part of the peroxide. No such increase of intensity of the nitrogen peroxide was found in the gases prepared with the help of ozone. This proves that the nitrogen peroxide formation is gradual and not instantaneous. As nitric oxide is only slowly oxidised by oxygen and quickly by ozone, it is conceivable, of course, that ozone accelerates the formation of nitrogen peroxide in the above experiment. This, however, cannot be the case, since the seventeen spark gaps only gave a yield 30 per cent. greater than the three spark gaps with ozone. Lowry believes that the nitrogen is not oxidised by the ozone, but that an active form of nitrogen is produced which is readily oxidised by ozone. It is interesting that Strutt's active nitrogen is not the same, since the latter when mixed with ozonised oxygen at low pressures and cooled with liquid air gives no trace of the oxides of nitrogen. It is not unreasonable to ask whether the production of nitrogen oxides in any form of electric discharge is not due to the interaction of active nitrogen and ozone or atomic oxygen.

Langmuir [47] claims to have prepared a chemically active form of hydrogen. If metallic filaments of tungsten, palladium, or platinum are heated to a high temperature in hydrogen at very low pressure (0·01 to 0·001 mm.) the hydrogen slowly disappears. It dissolves in the metals as hydrogen atoms, and these atoms appear to diffuse out, and then have little opportunity of joining together again to form molecules, owing to the high temperature and low pressure, and they are absorbed on the glass walls. Cooling the latter improves the yield. The maximum yield was 7·3 cu. mm. This hydrogen appears to be extraordinarily active, giving, for example, hydrogen phosphide with phosphorus. Hydro-

[47] *J. Amer. Chem. Soc.*, 1912, **34**, 1310; *A.*, ii, 1162.

gen phosphide was placed in the apparatus, and was entirely dissociated, the yellow deposit of phosphorus being clearly seen. This combined with the active hydrogen regenerating a certain amount of hydrogen phosphide.

Photochemistry.

Although perhaps this subject may be considered to fall more especially within the confines of physical chemistry, yet it is difficult to omit in a report on inorganic chemistry all reference to the extraordinarily interesting and important work which has been carried out during the past year on photochemical reactions between inorganic substances. There cannot be any doubt that this line of investigation promises to throw great light on the mechanism of chemical reactions and on the affinity relations of chemical compounds which are gradually being recognised as of fundamental importance as the driving force of all chemical processes. Marmier [48] has found that a dilute solution of sodium thiosulphate (containing less than 6 grams in 1 litre) is decomposed under the influence of light. The action of the light from a 240 watt lamp placed 6—8 cm. above such a solution is to produce sodium hyposulphite and some sulphur. After seventy minutes' exposure the solution was then found to contain only sodium sulphite. The light seemed to have no action if a stronger solution of thiosulphate was used.

Reynolds and Taylor [49] have carried out an important investigation on the decomposition of nitric acid by light, and they find that the reaction takes place according to the following equation:

$$4HNO_3 = 2H_2O + 2N_2O_4 + O_2.$$

The 100 per cent. acid when kept in the dark begins to decompose spontaneously after about one month. When, however, the acid contains water it is readily decomposed by light, and the reaction is reversible.

Winther [50] points out that under the influence of ultraviolet light ferrous chloride is oxidised by mercuric chloride according to the following equation:

$$2FeCl_2 + 2HgCl_2 = 2FeCl_3 + Hg_2Cl_2;$$

this reaction is reversible, but the reverse process moves very slowly indeed, unless it is so arranged as to give an electric current, when it proceeds much faster. Sometimes a potential difference of as much as 0·1 volt has been obtained with a current of 1 milliampere.

Boll and Job [51] have measured the change in conductivity of the

[48] *Compt. rend.*, 1912, **154**, 32; *A.*, ii, 112.
[49] *T.*, 1912, **101**, 131.
[50] *Zeitsch. Elektrochem.*, 1912, **18**, 138; *A.*, ii, 318.
[51] *Compt. rend.*, 1912, **154**, 881; *A.*, ii, 407.

hydrochloroplatinic acids produced on exposure to light. Very concordant results were obtained, which showed that the reaction was bimolecular. Matuschek and Nenning [52] find that many chemical reactions are accompanied by evolution of light. The reactions were caused to take place in a beaker, at the bottom of which a piece of tin foil cut in the form of a star was attached, the whole standing on a photographic plate. The following reactions were found to give out light: The action between sulphuric acid, hydrochloric acid, or nitric acid and copper, tin, or lead. Also during the solution of cupric oxide, cupric hydroxide, or potassium hydroxide in acids, the slaking of lime, the setting of cement and plaster, and the reaction between water and calcium carbide, there is an evolution of light. This work, however, has been criticised by Schneckenberg,[53] who says that the effects obtained are probably due to the photochemical action of the heat rays given out during the reaction on the photographic plate. Bennett [54] has investigated the photochemical reduction of copper sulphate solutions in the presence of reducing agents, the latter being present in quantity insufficient to cause the reduction to take place in the dark. In one set of experiments a dilute ethereal solution of phosphorus was added to the copper sulphate solution, and it was found that the precipitation of copper phosphide was obtained very much more quickly under the influence of light than in the dark; in fact, when the relative concentrations were properly balanced, the reduction would not take place in the dark at all, but took place readily under the influence of light.

Lewis [55] has investigated the photochemical decomposition of sodium hypochlorite solutions into sodium chloride and oxygen. The hypochlorite solution exhibits a marked absorption band in the ultraviolet region, and it would seem from the author's observations that this light in being absorbed produces the chemical change. Inasmuch as the reaction proceeds slowly in the dark, the phenomenon belongs to that class known as catalytic light reactions. In two papers [56] a theory was put forward which would seem to offer an explanation of the mechanism of photochemical reactions. Every atom in a chemical molecule possesses a certain amount of free affinity, and the force lines due to these free affinities must condense together with the escape of free energy. It therefore follows that the reactivity of such a condensed system is less than when the system is unlocked by some suitable means. This unlocking may be produced by the influence of a solvent or of light or of both together. Owing to the fact that the light is thereby

[52] *Chem. Zeit.*, 1912, **36**, 21; *A.*, ii, 116.
[53] *Ibid.*, 278.
[54] *J. Physical Chem.*, 1912, **16**, 782.
[55] *T.*, 1912, **101**, 2371.
[56] *Ibid.*, 1469, 1475.

doing work against chemical forces, the light will be absorbed. It follows naturally that the chemical reactivity of a molecular system may be materially increased under the influence of light of the right wave-length. This theory would also seem to explain the results obtained by Chapman [57] and his co-workers on the photochemical reactions of chlorine. One of the most striking results of this work is the inhibiting action of nitrogen chlorides on the union of hydrogen and chlorine. It would seem that these substances exert as great a negative catalytic action as water exerts a positive catalytic action on other reactions. Whilst this action of the nitrogen chlorides might conceivably be due to their power of absorbing the active light rays, yet it would seem far more probable that these substances have the power of preventing the opening of the closed force systems of the chlorine molecule by light. The writer would suggest that this may possibly be put to experimental proof. If a beam of light of fixed intensity be allowed to fall on a mixture of pure hydrogen and chlorine, the velocity of combination can be measured, and if the light be previously passed through a tube containing chlorine the velocity of combination will be decreased; then if a small quantity of nitrogen chloride be added to the chlorine in the first absorption vessel, the velocity of combination of the hydrogen and the chlorine in the second vessel should tend to increase.

Colloids.

Dumanski [58] describes the properties of colloidal arsenic trisulphide. It is a negatively charged colloid, which may be segregated by rapid centrifuging. The density of the material was found to be 2·938, and its specific conductivity to be 136×10^{-6}. The solution is coagulated by certain electrolytes, whilst others react with the sulphide; thus an iodine solution reacts according to the following equation:

$$As_2S_3 + 10I + 5H_2O = As_2O_5 + 10HI + 3S.$$

Similarly, a solution of potassium permanganate, decolorised by hydrogen peroxide, oxidises the sulphide to arsenic oxide, no coagulation taking place. Solutions of alkali hydroxides and of potassium cyanide have no coagulating action. On the other hand, silver nitrate and copper sulphate coagulate the colloid, but the precipitate contains considerable quantities of silver or lead. Lead acetate coagulates the colloid, but no lead sulphide is precipitated.

[57] For an excellent review of the work on the influence of light on the union of hydrogen and chlorine, see Chapman, *Science Progress*, 1912, **6**, 656; **7**, 66.

[58] *Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 262; *A.*, ii, 153.

J. Hoffmann [59] shows that the colour of ultramarine is due to colloidal sulphur, and that a number of compounds act as suitable solvents for colloidal sulphur. The silica in ultramarine can be replaced by boron trioxide without the disappearance of the blue colour. Furthermore, the colour does not greatly alter when the solvent is varied from $Na_2B_6O_{10}$ to $Na_2B_{10}O_{16}$. Potassium thiocyanate when dehydrated and heated to redness becomes blue, so here, again, a suitable solvent exists for the colloidal sulphur. Phosphoric oxide when fused at 900° with sodium sulphide gives a blue colour, which, however, disappears on cooling.

Hatschek [60] has carried out investigations into the production of substances in the gel of silicic acid. This acid is added to a 15 per cent. solution of sodium silicate, and after solidification of the silicic acid a hypertonic solution of a salt is added, the acid and the positive ion of the salt being so chosen that a salt separates out in the solid form within the gel. In this way lead chloride, and copper, calcium, and strontium phosphates were obtained in the crystalline form. In a second paper [61] the author deals with the reduction of gold in the silicic acid gel. Both solutions and gases were used as reducing agents. In the former case the reducing agent was poured over the gel which contained gold chloride, and in the latter case the gel in a test-tube was exposed to the gas. Under suitable conditions the gold was always deposited either in the gel or on the surface of the gel, or both at once, depending on the osmotic relationships. Furthermore, the gold was obtained in layers, and finally acetylene was found to give carbon and gold layers. The results, therefore, obtained are quite similar to the natural deposits which can therefore be explained in this way.

A certain amount of work has been done on the preparation of metallic sols and metallic organosols. Pappadà [62] describes the preparation of colloidal silver, gold, and platinum. These are negative colloids, and their reactions towards electrolytes are similar, but the most active of the three is silver. Amberger [63] describes the preparation of metal organosols. If lanolin, impregnated with the aqueous solution of the salt of a heavy metal, is triturated with a solution of alkali hydroxide, the hydroxide of the heavy metal in colloidal condition is obtained. If the oxides are readily reduced, then the colloidal metal may be obtained after the removal of water and all electrolytes. The residue will dissolve in any lanolin solvent, and on evaporation of this solvent solid sols with a high

[59] *Zeitsch. Chem. Ind. Kolloide*, 1912, **10**, 275 ; *A.*, ii, 752.
[60] *Ibid.*, 77 ; *A.*, ii, 449.
[61] *Ibid.*, 265 ; *A.*, ii, 772.
[62] *Ibid.*, 1911, **9**, 265, 270 ; *A.*, ii, 157, 169.
[63] *Ibid.*, 1912, **11**, 97, 100 ; *A.*, ii, 1053, 1059.

percentage of the metal are obtained. The lanolin acts as a protective colloid, and with the lanolin alcohols (cholesterol and *iso*cholesterol) sols can be obtained with an even higher metal content. Colloidal gold can be obtained in this way, hydrazine hydrate being used as reducing agent. The final product is soluble in ether, light petroleum, fats, and liquid paraffin to a solution having a deep blue colour, their solution in chloroform being reddish-violet. The addition of alcohol to the light petroleum solution precipitates a pasty product containing 84 per cent. of gold. Such products when dried are granular and golden-brown in colour. They dissolve easily in fats or liquid paraffin, but sparingly in ether or light petroleum.

Rare Earths.

Pure metallic cerium has been prepared by Hirsch[64] from the trichloride which is dehydrated, and then electrolysed after fusion in an iron crucible. The cerium thus obtained contains about 2 per cent. of impurities, for the most part iron and cerium oxide. In order to obtain the pure metal the impure product is amalgamated in boiling mercury, when the impurities may be skimmed off. The amalgam is then distilled in a quartz vessel lined with magnesia. The pure metal has a density of 6·92 at 25°, and is almost as soft and malleable as lead.

Dafert and Miklauz[65] have prepared the nitride and hydride of cerium. When metallic cerium is heated in a current of hydrogen it begins to absorb the gas at 310°, and the reaction is complete at 450°, cerium hydride being formed. This compound is dark blue or black, and is spontaneously inflammable in air. If moist air is passed over the substance no ammonia is formed, but when the substance spontaneously burns in air some nitride is formed, which gives ammonia with moisture. When the hydride is heated to from 800° to 900° in nitrogen the pure nitride is formed. This compound is not formed when cerium itself is heated in nitrogen; no ammonia is formed in the reaction, nor is there any ammonia formed when the nitride is heated in hydrogen. These authors were unable to obtain any evidence of the existence of imide compounds or of any compound of cerium with nitrogen and hydrogen.

Some doubt has been thrown by von Welsbach on the elementary character of both terbium and thulium. Welsbach himself does not appear to have continued these investigations, nor do they seem to have been criticised or denied by later workers. It would certainly seem that they merit further and independent investiga-

[64] *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 57; *A.*, ii, 258.
[65] *Monatsh.*, 1912, **33**, 911; *A.*, ii, 942.

tion. In one paper,[66] which deals with the fractional crystallisation of the double oxalates of the rare earths with ammonium, he says that the terbium is found distributed in the gadolinium and dysprosium fractions. The separation of the three elements is tedious, but may be carried out satisfactorily. The first and most insoluble product contains the gadolinium, whilst the final one contains the dysprosium. When optically tested these two fractions are found to be free from terbium. The oxides are coloured deep cinnamon or ochre, and they have peroxidic properties. In this way it may be seen that terbium has been resolved into more than one element. Exner and Haschek have shown that the spectrum of terbium contains many lines which are common to gadolinium and dysprosium. Von Welsbach repeated these spectroscopic tests, using much purer materials, and obtained the same results. The lines common to the three spectra were found to be so strong in the middle fraction as to leave no doubt as to the presence of these new elements. He calls them TbI and TbIII, the former being closely related to gadolinium and the latter to dysprosium. He points out that these two new elements, which are present in large amounts in the gadolinium and dysprosium fractions of the terbium series, should easily be separated.

Welsbach [67] has drawn a somewhat similar conclusion as regards thulium, which, from a spectroscopic point of view, he believes must consist of at least three elements.

Meyer and Goldenberg [68] have carried out an investigation on the properties of scandium oxide. They separate the thorium from scandium by the addition of potassium iodate, which is added in slight excess so that some scandium iodate was precipitated. Different specimens of scandium oxide freed in this way from thorium gave the atomic weight of scandium as 44·1—44·2. This agrees with Nilson's value. Meyer, Winter, and Speter,[69] on the other hand, using scandium which had been purified from thorium by the sodium carbonate method, found the atomic weight to be 45. Meyer and Goldenberg investigated the arc spectrum of the scandium oxide fractions which had atomic weight 44 and 45 respectively, and they found that there was no difference between them. They conclude, therefore, that the method is not delicate enough for the detection of 0·5 per cent. of thorium. The magnetisation-coefficient, however, affords a much more delicate test, as the scandium oxide (atomic weight = 45) gives a value of $+0{\cdot}04 \times 10^{-6}$,

[66] *Chem. Zeit.*, 1911, **35**, 658.
[67] *Monatsh.*, 1911, **32**, 373 ; *A.*, 1911, ii, 607.
[68] *Chem. News*, 1912, **106**, 13 ; *A.*, ii, 768.
[69] *Zeitsch. anorg. Chem.*, 1910, **67**, 398 ; *A.*, 1910, ii, 854.

whilst the scandium oxide (atomic weight = 44) gives a coefficient of $-0{\cdot}12 \times 10^{-6}$. Scandium is diamagnetic, as also are lanthanum and yttrium, which also belong to group III in the periodic table.

Some interesting experiments have been carried out by Joye and Garnier [70] on the hydrated oxides of neodymium. It is well known that neodymium hydroxide gives a different reflection spectrum from neodymium oxide. By heating the hydroxide to various temperatures and observing the spectra, they have succeeded in establishing the existence of two new hydrates, namely, $2Nd_2O_3,3H_2O$ and $2Nd_2O_3,2H_2O$. The first of these is formed at 310—325°, and the second at 525°.

Urbain and Bourion [71] have succeeded in preparing europous chloride by reducing europic chloride in hydrogen at 400—450°. It is a colourless, amorphous compound, which is soluble in water to a neutral solution. At 100° the solution oxidises according to the equation:

$$12EuCl_2 + 3O_2 = 8EuCl_3 + 2Eu_2O_3.$$

The europous chloride is more stable than the corresponding samarium compound, which is the only other lower chloride known in the group.

Two papers have been published dealing with isomorphic series of salts of the rare earths. In the first of these, Billows [72] describes the preparation of a complex molybdate having the composition $(NH_4)_6R_2Mo_{14}O_{28},24H_2O$, where R = Ce, La (Ce La), Nd, Pr, Sm. He found that all these crystallise in the triclinic system, and are perfectly isomorphous. In the second paper, Jantsch [73] has described the double nitrates of formula $M'''(NO_3)_6M_3'',24(H_2O)$, where M''' = La, Ce, Pr, Nd, Sa, Gd, and M'' = Mg, Zn, N, Co, Mn. The only exception is the double nitrate of gadolinium and manganese, which is too soluble to crystallise well. All the other salts are isomorphous, and crystallise well; all melt in their water of crystallisation at definite temperatures, and these temperatures fall as the elements are substituted in both series in the order in which they are given above. The solubilities follow the same order, the magnesium salts being the least soluble. The cerium double salts, however, are less soluble than those of lanthanum. The molecular volume curves show close parallelism in the case of the magnesium, manganese, nickel, cobalt, and zinc salts. The molecular volume of the cobalt salts is greater than that of the nickel salts, and that of the neodymium salts greater than that of the praseo-

[70] *Compt. rend.*, 1912, **154**, 510; *A.*, ii, 352.
[71] *Ibid.*, 1911, **153**, 1155; *A.*, ii, 162.
[72] *Zeitsch. Kryst. Min.*, 1912, **50**, 500; *A.*, ii, 560.
[73] *Zeitsch. anorg. Chem.*, 1912, **76**, 303; *A.*, ii, 767.

dymium salts, so that in both cases the order is the reverse of that which would be expected from the periodic law.

A considerable amount of work has been carried out on the rare earths by James and his colleagues.[74] In one paper are described the preparation and properties of the salts of samarium and neodymium of a very large number of organic acids, mainly sulphonic acids of the aliphatic series. This formed part of a search for satisfactory salts for the purposes of fractionation. In two other papers,[75, 76] the application of sebacic acid is described for the quantitative precipitation of thorium and yttrium. In the case of thorium an aqueous solution of the acid is added to a neutral solution of the thorium salt, when thorium sebacate is precipitated. This method can be used for the quantitative separation of thorium in the presence of cerium, lanthanum, praseodymium, neodymium, samarium, and gadolinium. It is also of value for the separation and purification of thorium. Pyrotartaric acid may also be used, and when added to a cold neutral solution of the thorium salt no precipitate is obtained, but, on boiling, the thorium pyrotartrate is quantitatively precipitated. In the case of yttrium the element may be quantitatively separated from certain other elements as follows: A single precipitation with ammonium sebacate gives a quantitative separation of yttrium from sodium, whilst a double precipitation gives a precipitate completely free from potassium. On the other hand, oxalic acid gives the most satisfactory separation of yttrium from iron, aluminium, lithium, and magnesium. Finally, James[77] has described a complete scheme for the separation of the rare earths from one another. This scheme is, of course, far too long to be detailed in this report, but no account of the progress of work done in this field of research would be complete without including, at any rate, this brief mention.

Group I.

Ermen[78] has investigated certain basic salts of copper, and he finds that, with $N/10$-solutions, the addition of sodium hydroxide to copper sulphate until all the copper is precipitated, or the addition of copper sulphate to sodium hydroxide until the copper just appears in the solution, two molecules of copper sulphate and three molecules of sodium hydroxide always react together. The blue basic sulphate, $CuSO_4,3Cu(OH)_2$, is precipitated, the same com-

[74] James, Hoben and Robinson, *J. Amer. Chem. Soc.*, 1912, **34**, 276, 281; *A.*, i, 233.

[75] Smith and James, *ibid.*, 281; *A.*, ii, 390.

[76] Whittemore and James, *ibid.*, 772; *A.*, ii, 690.

[77] *Ibid.*, 757; *A.*, ii, 690.

[78] *J. Soc. Chem. Ind.*, 1912, **31**, 312; *A.*, ii, 453.

pound being obtained if the sodium hydroxide solution is added to the solution of copper sulphate when boiling. On the other hand, the addition of copper sulphate to a boiling hydroxide solution precipitates the black oxide of copper, which is not completely converted into the basic salt even on prolonged boiling. Evidence was also obtained of the existence of a green basic salt containing 3·5 of copper and 1 of SO_4. On mixing cold dilute solutions of copper sulphate and sodium carbonate, one molecule of each salt reacts together, and the blue basic carbonate, $CuCO_3,Cu(OH)_2,H_2O$, is precipitated. On keeping, this compound changes into malachite, $CuCO_3,Cu(OH)_2$. From this substance sodium hydroxide removes all the carbon dioxide. When sodium carbonate solution is run into a boiling solution of copper sulphate, the blue compound, $CuSO_4,3Cu(OH)_2$, is also obtained. When copper sulphate is added to aqueous ammonia until a permanent precipitate is produced, one molecule of copper sulphate is found to have reacted with four molecules of ammonia. The addition of more copper sulphate until the solution becomes colourless gives the compound $CuSO_4,2Cu(OH)_2$. If an aqueous solution of copper sulphate is saturated with ammonia gas a precipitate is obtained having the composition $CuSO_4,4NH_3,H_2O$. This substance is also formed by triturating copper sulphate crystals with strong aqueous ammonia, or by adding anhydrous copper sulphate to strong ammonia solution. It is also obtained by exposing the compound $CuSO_4,5NH_3$ to moist air.

Cumming and Gemmell[79] have investigated the trihydrate of copper nitrate. It is best prepared by dissolving cupric oxide in concentrated nitric acid. The salt may be recrystallised from hot concentrated nitric acid, and may be dried on a porous tile over potassium hydroxide. If the nitric acid is obtained by distillation from sulphuric acid in a current of carbon dioxide, the cupric oxide reacts with it at a temperature of 70—75°. Nitrogen peroxide and oxygen are evolved, the process taking place according to the equation:

$$CuO + 6HNO_3 = Cu(NO_3)_2,3H_2O + 4NO_2 + O_2.$$

The hexahydrate of copper nitrate when dried in a vacuum over phosphoric oxide readily loses three molecules of water, giving the trihydrate. It would appear that the only basic nitrate of copper is $Cu(NO_3)_2,3Cu(OH)_2$, and this may readily be prepared by heating the trihydrate to 100° or by boiling a concentrated aqueous solution of copper nitrate with cupric oxide. The transition temperature between the two hydrates of copper nitrate has been found to be 24·66° with the dilatometer and 24·65° thermometrically.

[79] *Proc. Roy. Soc. Edin.*, 1912, **32**, 4; *A.*, ii, 556.

Baubigny[80] finds that on heating copper sulphate solution with an excess of sodium sulphite solution so that the precipitate first formed is redissolved, and if the resulting colourless solution is heated on a water-bath, a red precipitate is formed, which is a double compound of sodium sulphite and cuprous sulphite, whilst the solution contains sodium dithionate. The process takes place according to the equation:

$$2CuSO_4 + 4Na_2SO_3 = 2Na_2SO_4 + Cu_2SO_3,Na_2SO_3 + Na_2S_2O_6.$$

If aqueous solutions of copper sulphate and sodium sulphite are mixed in a sealed tube at the ordinary temperature, then after some hours colourless crystals are formed having the constitution $Cu_2SO_3,Na_2SO_3,12H_2O$.

Some interesting work has been carried out by D'Ans and Friederich[81] on the preparation of derivatives of hydrogen peroxide, in which the hydrogen atoms have been partly replaced by sodium or potassium. An ethereal solution of pure hydrogen peroxide reacts with metallic sodium to give a white solid having the formula $2NaHO_2,H_2O_2$. This compound is identical with that prepared from the action of hydrogen peroxide on sodium ethoxide.[82] Metallic potassium acts more vigorously than sodium, and gives a substance having the formula $2KHO_2,3H_2O_2$. When an absolute alcoholic solution of potassium hydroxide and hydrogen peroxide are mixed they then give $2KHO_2,H_2O_2$, a compound which has previously been obtained by Schöne.[83]

The phosphides of cæsium, rubidium, potassium, and sodium having the general formula M_2P_5 have been studied by Hackspill and Bossuet.[84] Two or three grams of the metal and a large globule of phosphorus are distilled successively into an exhausted tube, and the mixture heated to 400—500°. The black mass thus obtained still contains free metal, but after continuing the heating for about one hundred and fifty hours this is volatilised, and the phosphide appears reddish-brown. At temperatures between 0° and 100° the four compounds resemble cadmium sulphide in colour, they become darker at higher temperatures, and are almost colourless at the temperature of boiling nitrogen. They melt at 650° with loss of phosphorus. They decompose in air, and when treated with water give a solid hydride of phosphorus with a small amount of hydrogen phosphide and hydrogen.

Barbieri[85] claims to have prepared a compound containing

[80] *Compt. rend.*, 1912, **154**, 434, 701; *A.*, ii, 351, 447.
[81] *Zeitsch. anorg. Chem.*, 1912, **73**, 325; *A.*, ii, 151.
[82] Wolffenstein and Peltner, *Ber.*, 1908, **41**, 280; *A.*, 1908, ii, 180.
[83] *Annalen*, 1878, **193**, 276, 289; *A.*, 1878, 931.
[84] *Compt. rend.*, 1912, **154**, 209; *A.*, ii, 252.
[85] *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 560; *A.*, ii, 763.

bivalent silver. If a solution of silver nitrate in pyridine is added to a cold solution of potassium persulphate, a yellow precipitate is obtained, with the formula $AgS_2O_8,4C_5NH_5$, and the substance resembles the corresponding cupric compound. If very dilute solutions are used the silver and copper compounds can be precipitated simultaneously, and, by varying the proportions of the silver and copper, mixed crystals are formed, showing complete gradations of colour between the orange silver compound and the violet cupric compound, thus proving the complete isomorphism of the two.

Group II.

Barre[86] has prepared the double carbonates of calcium with sodium and potassium. If precipitated calcium carbonate is boiled with a concentrated solution of sodium carbonate, orthorhombic crystals are formed of $Na_2CO_3,CaCO_3,2H_2O$. At 98° the compound is not formed unless the solution contains at least 21·06 per cent. of sodium carbonate. Under the same conditions potassium carbonate gives prismatic needles of $K_2CO_3,CaCO_3$, which are readily hydrolysed by water, and are only stable in a solution containing at least 59·25 per cent. of potassium carbonate.

Niederstadt[87] has shown that aragonite and calcite may be distinguished in that the former is readily coloured lilac by cobalt salts, whilst the latter only assumes a bright blue colour on prolonged boiling. Aragonite is the more active towards manganese, zinc, and iron salts, whilst calcite more readily precipitates copper, lead, and silver.

Group III.

An important paper has been published by Travers and Ray[88] on borohydrates. Magnesium powder is heated with boron trioxide to a bright red-heat in a current of hydrogen. When the resulting powder is treated with water a yellow solution is obtained, which has powerful reducing properties; it is slightly alkaline to litmus, and on boiling it gives off hydrogen. The addition of dilute acid causes an evolution of hydrogen, together with a trace of some boron compound. The original solution both before and after the addition of acid is strongly reducing. It takes up iodine, and precipitates the heavy metals from solutions of their salts. The authors find that the amount of hydrogen evolved on the addition of acid and the iodine equivalent are in the ratio of 1 to 1 or 1 to 2,

[86] *Compt. rend.*, 1912, **154**, 279; *A.*, ii, 254.
[87] *Zeitsch. angew. Chem.*, 1912, **25**, 1219; *A.*, ii, 760.
[88] *Proc. Roy. Soc.*, 1912, A, **87**, 163; *A.*, ii, 938.

and analyses show figures that are very near to one or the other of these ratios. Furthermore, the solutions contain one atom of boron for every atom of hydrogen that is evolved when the solution is treated with acid. When the aqueous solutions are evaporated in a vacuum at low temperatures with the help of a condenser cooled in liquid air, little or no gas is evolved until all the water has been distilled off. A viscous residue is left, which now proceeds to give off hydrogen rapidly, and then sets to a semi-crystalline or glassy solid. The amount of hydrogen evolved at this stage is equal to half the volume of hydrogen which is given off when the original solution is acidified. If the bulb containing the glassy solid is left connected to the pump, a further quantity of hydrogen is slowly evolved, and the amount of this second quantity of hydrogen is equal to the first quantity. On gently heating the substance a third quantity of hydrogen is evolved, which again is about equal to the two amounts previously evolved. It is found that half the boron distils over during the evaporation, and as the distillate does not take up much iodine the authors conclude that this volatile boron compound is oxidised. They carried out certain experiments which proved that this volatile boron compound is not boric acid, and put forward the view that a polymeride of boron trioxide exists which is not acid, and is volatile; they suggest that the original substances are hydrated derivatives of B_4O_2 and B_4O_3.

A second important paper has appeared during the year, namely, one dealing with the hydrides of boron, by Stock and Massenez.[89] These authors prepared the hydrides from magnesium boride, and some difficulty was experienced in the preparation of this compound so as to obtain a good yield of the boron hydrides. The best result is obtained as follows: one part of very finely powdered boron trioxide is intimately mixed with three parts of magnesium powder, and 10 grams of the mixture are rapidly heated in a thin iron crucible in a stream of hydrogen. The powdered product is slowly dropped into not too dilute hydrochloric acid at 50—80°. The gas evolved is fractionated by means of liquid air. Two hydrides were isolated, namely, B_4H_{10} and B_6H_{12}. The former was analysed by treatment with water, when the following reaction takes place:

$$B_4H_{10}+12H_2O=4B(OH)_3+11H_2.$$

The results of the analysis and the density determinations agreed with the formula B_4H_{10}. The compound B_6H_{12} was analysed in a somewhat similar way, and its density was also determined, but owing to the small quantities available there is still some doubt as to the number of hydrogen atoms in the molecule.

The hydride B_4H_{10} melts at $-112°$, and boils between 16° and

[89] *Ber.*, 1912, **45**, 3539; *A.*, 1913, ii, 44.

17°/760 mm. The hydride B_6H_{12} should boil at about 100°, but both compounds are unstable, and tend to decompose at the ordinary temperature, and give a series of further hydrides yet to be investigated. The hydride B_4H_{10} is rapidly absorbed by alkali, and the solution slowly evolves hydrogen, the complete reaction being similar to that with water mentioned above. The hydride B_6H_{12}, on the other hand, gives up hydrogen immediately when treated with alkali.

Johnson [90] has found that the alumina formed by dehydrating the hydroxide at low temperatures is an excellent drying agent for gases such as hydrogen phosphide, hydrogen bromide, and hydrogen iodide, where phosphoric oxide is useless. It is better than calcium bromide, zinc bromide, or zinc chloride, and is more efficient than sulphuric acid. A tube filled with this alumina can be used indefinitely, as the substance can readily be dried again by heating with a smoky flame in a stream of air dried by sulphuric acid.

Terni [91] has prepared a peroxide of aluminium by adding an excess of 30 per cent. solution of hydrogen peroxide to aluminium hydroxide dissolved in the minimum quantity of 50 per cent. solution of potassium hydroxide. An amorphous, white powder is formed, having a constitution $Al_2O_3,Al_2O_4,10H_2O$. It is a true peroxide, and Terni believes that the first product of the reaction is Al_2O_4, which is changed by hydrolysis to the above substance.

Bosshard and Zwicky [92] have investigated the perborates. Twenty of these compounds were heated to a temperature of 55—65°, either under diminished pressure or in a current of air free from carbon dioxide. In only one case was a trace of hydrogen peroxide found in the distillate. Usually the water of crystallisation distilled over, and the percentage of active oxygen in the salt was increased. Potassium peroxide perborate when dissolved in water evolves only traces of oxygen, and when dried in a vacuum over phosphoric oxide four molecules of the salt lose one molecule of water, so it is improbable that the salt contains hydrogen peroxide of crystallisation. Further, it is found that sodium perborate evolves oxygen when treated with colloidal platinum solution more slowly than hydrogen peroxide solution under the same conditions. The authors conclude, therefore, that the perborates do not contain hydrogen peroxide of crystallisation, and that they have the constitution:

$$M\cdot O\cdot B<\begin{matrix}O\\|\\O\end{matrix} \quad \text{and not} \quad M\cdot O\cdot O\cdot B:O.$$

[90] *J. Amer. Chem. Soc.*, 1912, **34**, 911 ; *A.*, ii, 847.
[91] *Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 104 ; *A.*, ii, 944.
[92] *Zeitsch. angew. Chem.*, 1912, **25**, 993 ; *A.*, ii, 640.

According to this the potassium salt mentioned above would have the constitution $K{\cdot}O{\cdot}O{\cdot}B{<}^{O}_{O}$, and not $K{\cdot}O{\cdot}O{\cdot}O{\cdot}B{:}O$, as, owing to the three oxygen atoms existing in the chain, a compound of the latter constitution would probably be very unstable. They point out that Riesenfeld's test (see under Group IV) fails with perborates.

Group IV.

A certain amount of work on silicon hydride has to be reported. Adwentowski and Drozdowski [93] state that pure silicon hydride, SiH_4, can only be prepared by repeated fractionation of the gas usually obtained. By the action of hydrogen chloride on magnesium silicide a gas is produced from which liquid fractions are obtained, which are mixtures of several silicon hydrides. The pure SiH_4 is spontaneously inflammable in plenty of air. The weight of one litre is 1·4538 grams. It boils at $-116°/740$ mm. Its critical temperature is $-3·5°$, and its critical pressure is 47·8 atmospheres.

Besson [94] describes certain reactions of silicon tetrahydride. Powdered magnesium with half its weight of powdered quartz is stamped into a crucible and fired by the ignition of some powdered magnesium placed on the top of the mixture. The magnesium silicide obtained when treated with hydrogen chloride gives a gas containing 6—7 per cent. of SiH_4. A gas containing less than 0·5 per cent. is not spontaneously inflammable, but fumes in moist air, giving a colourless solid, which varies in composition between $H_4Si_2O_3$ and $H_4Si_2O_4$. In his second paper Besson points out that the gas from the magnesium silicide contains hydrogen phosphide and hydrogen sulphide as impurities. These impurities are readily removed by passing the gas through a dilute solution of iodine in potassium iodide or hydriodic acid, and the gas may then be dried with phosphoric oxide. During the preparation silico-oxalic acid, $H_2Si_2O_4$, separates as a white solid in the reaction mixture, the amount of this being from 25 to 30 per cent. of the weight of the magnesium used. The dry gas is not acted on by light, but under the influence of the electric discharge it gives a yellow to brown solid deposit of uncertain composition, which is spontaneously inflammable in air. The gas has no action on concentrated ammonia solution or liquid ammonia when dry. In the presence of moisture it gives with liquid ammonia a white solid, which when dried at 100° has the composition $H_4Si_3O_7$. If the white solid

[93] *Bull. Acad. Sci. Cracow*, 1911, A, 330; *A.*, ii, 44.
[94] *Compt. rend.*, 1912, **154**, 116, 1603; *A.*, ii, 256, 641.

obtained when the gas fumes in moist air is dried at 100° in a vacuum for several hours, it has the composition $H_3Si_3O_5$. When carefully heated in a vacuum it loses hydrogen, and the composition of the residue approximates to Si_3O_5.

Riesenfeld and Mau [95] discuss the constitution of the percarbonates, and they differentiate between the true percarbonate and the ordinary carbonate containing hydrogen peroxide of crystallisation. Whilst the former give a quantitative separation of iodine from neutral potassium iodide solution, the latter liberate practically no iodine.[96] Even the addition of hydrogen peroxide to a solution of potassium percarbonate in the proportion of 2 molecules to 1 causes very little change in the quantity of iodine liberated. A solution of potassium percarbonate at 15°, after keeping for an hour, still liberates iodine quantitatively from potassium iodide solution, whilst the so-called sodium percarbonate does not liberate iodine either at 15° or 0° or even when added as a solid. The authors conclude that the latter possesses the constitution

$$Na_2CO_3,H_2O_2,\tfrac{1}{2}H_2O.$$

Similarly, Peltner's [97] rubidium percarbonate must have the formula $Rb_2CO_3,3H_2O_2$. They also point out that persulphates and sulphates with hydrogen peroxide of crystallisation [98] react towards potassium iodide in a similar way to the percarbonates. In their opinion, therefore, this reaction may be considered as a general one for the differentiation between true per-salts and salts containing hydrogen peroxide of crystallisation. It may be pointed out, however, that the test fails in the case of the perborates (see under Group III). Based on the experience gained from these results, Riesenfeld and Mau have investigated the salts formed by the action of carbon dioxide on sodium peroxide. The four salts prepared by Wolffenstein and Peltner [99] are found by Riesenfeld and Mau to be really salts of two different acids, namely, monoperoxycarbonic, H_2CO_4, and monoperoxydicarbonic acid, $H_2C_2O_6$, and to have the constitution $Na_2CO_4,Na_2CO_4,H_2O_2,Na_2C_2O_6$ and

$$Na_2C_2O_6,H_2O_2.$$

They prove this conclusion by comparing the reactions of the four salts with potassium iodide. They also found that the two pairs of salts were mutually convertible by the addition or withdrawal of hydrogen peroxide. It was observed that the potassium percarbonate, $K_2C_2O_6$, prepared by electrolytic methods, behaves differently

[95] *Ber.*, 1911, **44**, 3589, 3595; *A.*, ii, 156.

[96] Compare Reisenfeld and Reinhold, *ibid.*, 1909, **42**, 4377; Tanatar, *ibid.*, 1910, **43**, 127, 2149; Reisenfeld, *ibid.*, 566, 2594; *A.*, 1910, ii, 33, 203, 290, 774, 952.

[97] *Ibid.*, 1909, **42**, 1777; *A.*, 1909, ii, 574.

[98] Willstätter, *ibid.*, 1903, **36**, 1828; *A.*, 1903, ii, 537.

[99] *Ber.*, 1908, **41**, 280; *A.*, 1908, ii, 180.

towards potassium iodide from the corresponding sodium compounds, for the potassium salt gives a quantitative liberation of iodine, whereas in the case of the sodium salt only about 50 per cent. of its active oxygen liberates iodine. By the action of carbon dioxide on potassium peroxide a compound, $K_2C_2O_6$, was formed which behaves towards potassium iodide solution similarly to the sodium compound. This compound, therefore, must be isomeric with ordinary potassium percarbonate, and they suggest that its constitution may be represented by K·O·O·CO·O·CO·O·K, as distinct from KO·CO·O·O·CO·OK.

Stock and Praetorius [1] have contributed considerably to our knowledge of carbon subsulphide, C_3S_2, first prepared by von Lengyel.[2] A modification of von Lengyel's method was used in its preparation. An electric arc is maintained with 10 to 15 amperes at 110 volts under pure carbon disulphide between a graphite cylinder as cathode and an anode of graphite and antimony. Finely powdered antimony and graphite were mixed with sugar solution, and pressed into rods, which after being dried were heated to carbonise the sugar. A slow stream of carbon dioxide was passed through the apparatus, and the resulting fluid was shaken with mercury and some phosphoric oxide to remove the sulphur. When the carbon disulphide had been distilled off, the subsulphide was sublimed in a high vacuum using a condenser cooled with liquid ammonia. At the ordinary temperature C_3S_2 forms a clear, red, strongly refractive liquid, and in dilute carbon disulphide solution it exhibits an absorption band between 530 and 455 $\mu\mu$. Under the influence of light it polymerises finally into a black substance, which is unaffected by water, hydrochloric acid, sodium hydroxide solution, or chlorine water. The subsulphide reacts at once with aniline to give thiomalonamide:

$$C_3S_2 + 2C_6H_5\cdot NH_2 = CH_2(CS\cdot NH\cdot C_6H_5)_2.$$

It is clearly the analogue of carbon suboxide, C_3O_2.

Group V.

During the year Franklin has published four papers describing the preparation and properties of certain amine compounds, thus continuing his work based on his ammonia system of acids, bases, and salts. In a series of papers [3] in previous years he has pointed out the analogy between liquid ammonia and water as electrolytic

[1] *Ber.*, 1912, **45**, 3568; *A.*, 1913, ii, 46.

[2] *Ibid.*, 1893, **26**, 2690; *A.*, 1894. ii, 90.

[3] Franklin and Kraus, *Amer. Chem. J.*, 1899, **21**, 1, 8; 1900, **23**, 277; Franklin and Stafford, *ibid.*, 1902, **28**, 83; Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820; *A.*, 1899, ii, 284; 1900, ii, 382; 1902, i, 748; 1905, ii, 581.

solvents, and the analogy between the reactions which take place in the two solvents. He formulated a system of acids, bases, and salts on the basis of ammonia as the typical substance, analogous to the ordinary system of oxygen acids, bases, and salts as derivatives of water. During the present year the system has been further developed, and the relationships have been shown to be fully justified. In the first paper[4] he describes the preparation of potassium ammoniocadmiate, $Cd(NHK)_2,2NH_3$, which is obtained by adding potassamide to cadmium iodide or nitrate dissolved in liquid ammonia. This substance corresponds with the zinc compound described by Fitzgerald.[5]

In a second paper[6] Franklin and Hine describe the reaction between titanium nitride bromide and potassamide in liquid ammonia, which, although the analyses show that absolutely pure products were not obtained, would certainly seem to take place according to the equation:

$$N{:}Ti{\cdot}Br + 2KNH_2 = N{:}Ti{\cdot}NHK + KBr + NH_3.$$

In a third paper[7] Franklin describes the action of potassamide on a liquid ammonia solution of $Cu(NO_3)_2,4NH_3$. These compounds react according to the equation:

$$3Cu(NO_3)_2 + 6KNH_2 = Cu_3N,nNH_3 + 6KNO_3 + (4-n)NH_3 + N.$$

The copper compound is precipitated, and when warmed to the laboratory temperature in a vacuum it is converted into cuprous imide, Cu_2NH, and when heated to 160°, cuprous nitride, Cu_3N, is formed. The compounds with the general formula Cu_3N,nNH_3 readily dissolve in liquid ammonia solution of potassamide, and in this way well-crystallised specimens of a colourless compound having the formula $CuNK_2,3NH_3$ were obtained. This potassium ammoniocuprite with three molecules of ammonia of crystallisation loses one molecule of ammonia in a vacuum at the ordinary temperature, and at higher temperatures it loses a further molecule, forming $CuNK_2,NH_3$.

In a fourth paper[8] Franklin describes the preparation of the corresponding thallium compounds. When a liquid ammonia solution of potassamide is added to a liquid ammonia solution of a thallous salt, a black precipitate of thallium nitride is formed; thus, with thallous nitrate the reaction takes place according to the equation:

$$3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3.$$

[4] *Amer. Chem. J.*, 1912, **47**, 285; *A.*, ii, 451.
[5] *J. Amer. Chem. Soc.*, 1907, **29**, 656; *A.*, 1907, ii, 546.
[6] *Ibid.*, 1912, **34**, 1497; *A.*, ii, 1168.
[7] *Ibid.*, 1501; *A.*, ii, 1174.
[8] *J. Physical Chem.*, 1912, **16**, 682; *A.*, 1913, ii, 52.

This precipitate readily dissolves in a liquid ammonia solution of ammonium nitrate or potassamide, and so must be assumed to be amphoteric in character. When it is dissolved in a liquid ammonia solution of potassamide, a yellow solution is formed, from which yellow crystals of the compound, $TlNK_2,4NH_3$, may be obtained. This potassium ammoniothallate readily loses portions of its ammonia of crystallisation, giving the compounds $TlNK_2,2NH_3$ and $TlNK_2,1\frac{1}{3}NH_3$. When excess of potassamide is used, well-crystallised products are obtained, which are impossible of formulation as definite chemical compounds. Franklin looks upon these as isomorphous mixtures of the compound $TlNK_2,4NH_3$ with potassamide, or perhaps rather an isomorphous mixture of the unknown thallous amide and potassamide. Considerable difficulty was found in the work owing to the great instability of these compounds. They explode violently when heated or subjected to shock, and their satisfactory analysis was a matter of considerable difficulty.

Dafert and Miklauz[9] have made investigations on the amide, imide, and nitride of lithium. Under the influence of sunlight lithiumimide decomposes with the production of a dark red colour, the reaction being represented by the equation:

$$2Li_2NH = Li_3N + LiNH_2.$$

They find that by the action of nitrogen on lithium hydride, hydrogen on lithium nitride, a mixture of nitrogen and hydrogen or of ammonia on lithium hydride or nitride, lithium-imide, -amide, or trilithiumamide, or mixtures of these compounds are formed according to the temperature and other conditions. Lithiumamide is formed by the action of ammonia on amorphous lithium nitride at 130—350°, or on crystalline lithium nitride at 410—430°, or on lithium hydride at 440—460°, thus:

$$Li_3N + 2NH_3 = 3LiNH_2 \text{ or } LiH + NH_3 = LiNH_2 + H_2.$$

At 450° hydrogen reacts with lithiumimide according to the equation:

$$2H_2 + 3Li_2NH = 2Li_3NH_2 + NH_3.$$

The trilithiumamide when heated to 600° in a stream of nitrogen reacts according to the equation:

$$4Li_3NH_2 + N_2 = 6Li_2NH + H_2.$$

Ruff and Martin[10] have prepared metallic vanadium in a high state of purity. A mixture of vanadium trioxide and carbon are moulded with starch into rods, and these are sintered in an electric furnace at 1750°, and finally fused in the arc. The product contains 95 to 97 per cent. of vanadium. Vanadium carbide can be prepared

[9] *Monatsh.*, 1912, **33**, 63; *A.*, ii, 253.

[10] *Zeitsch. anorg. Chem.*, 1912, **25**, 49; *A.*, ii, 166.

in the resistance furnace. It is silvery-white, highly crystalline, and very hard. It melts at 2750°. This carbide if powdered and mixed with the trioxide and a little starch solution, and then heated to 1950° in a zirconia crucible, gives the fused metal, which on analysis is found to contain 98 per cent. of vanadium and 1·91 per cent. of carbon. The authors find that the pure metal melts at 1715°.

Renschler [11] has shown that ammonium metavanadate can readily be reduced electrolytically to tervalent vanadium salts. The cathode is placed in a porous cell; both the anode and cathode are lead cylinders, and dip in 50 per cent. sulphuric acid. Ammonium vanadate is added to the cathode cell, and the liquid well stirred, and a current of 4 amperes passed through until the solution becomes green. It is then removed and kept, when ammonium vanadium alum separates in good yield.

Group VI.

Von Pirani and Meyer [12] have determined the melting points of tungsten and molybdenum, finding that tungsten melts at $3100° \pm 60°$ and molybdenum at $2450° \pm 30°$.

Ruder [13] has studied the action of acids and alkalis on wrought tungsten and molybdenum. He finds that both metals are somewhat resistant to acids owing to the formation of a coating of oxide. Tungsten is most rapidly attacked by fuming sulphuric acid, but only 1·2 per cent. dissolves in eight hours. Molybdenum is more easily attacked than tungsten, but it is fairly resistive to concentrated hydrochloric acid below 125°, and is not affected by hydrofluoric acid. The metals are not attacked by aqueous potassium hydroxide, but are slowly dissolved by fused alkali.

Sanger and Riegel [14] have succeeded in preparing pyrosulphuryl chloride and chlorosulphonic acid in the pure state. In the preparation of the former a mixture of fuming sulphuric acid and sulphur trioxide is added gradually to an excess of carbon tetrachloride in a heated flask, when the following reaction takes place:

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2,$$

but some chlorosulphonic acid is also formed at the same time. The liquid is purified by repeated fractional distillation off sodium chloride.

The pure pyrosulphuryl chloride boils at 152·5—153°/760 mm.

[11] *Zeitsch. Elektrochem.*, 1912, **18**, 137; *A.*, ii, 356.

[12] *Ber.*, 1912, **14**, 426; *A.*, ii, 560.

[13] *J. Amer. Chem. Soc.*, 1912, **34**, 387; *A.*, ii, 454.

[14] *Proc. Amer. Acad.*, 1912, **47**, 673; *Zeitsch. anorg. Chem.*, 1912, **76**, 79; *A.*, ii, 752.

Chlorosulphonic acid is obtained by passing dry hydrogen chloride into a mixture of sulphuric acid and sulphur trioxide, the mixture is distilled in a stream of hydrogen chloride, and the fraction passing over between 145° and 160° is collected. It is purified by fractional distillation at low temperatures. It boils at 151—152°/765 mm. and at 74—75°/19 mm. The two compounds may readily be distinguished, as powdered selenium or tellurium give colours with chlorosulphonic acid and not with pyrosulphuryl chloride.

Group VII.

A further investigation into the reactions of bleaching powder has been carried out by Taylor and Bostock.[15] When bleaching powder and thirty times its weight of water is distilled with sulphuric acid, hydrochloric acid, or nitric acid in quantity slightly greater than is necessary to neutralise the free lime present, hypochlorous acid, and a small quantity of chlorine are evolved. When the quantity of acid is sufficient to neutralise all the free lime and to decompose all the hypochlorite theoretically present, the proportion of chlorine evolved is considerably greater. With more acid the quantity of chlorine is still further increased until finally nothing but chlorine is evolved. There is no marked difference between the results obtained with each of the three acids present. Acetic and phosphoric acids are very much alike in their action, but they differ considerably from the mineral acids in their behaviour to bleaching powder. Even with large amounts of these acids the proportion of hypochlorous acid does not fall much below 50 per cent. When bleaching powder is distilled with boric acid and sufficient water, almost pure hypochlorous acid is produced. There is very little difference, even if three parts of boric acid are employed to one of bleaching powder. The authors suggest this as a very convenient method for the preparation of aqueous hypochlorous acid.

If carbon dioxide is bubbled through a mixture of bleaching powder and water at the ordinary temperature nothing but chlorine is evolved; when, however, the solution is warm, hypochlorous acid comes off in an amount increasing with the temperature, until when the mixture is boiled hypochlorous acid is evolved practically free from chlorine.

Higgins[16] has contributed a further important paper on the process of bleaching, and he finds that the action is due to both hypochlorous acid and hypochlorites. Since the former is less stable than the latter it possesses a greater bleaching effect. Hence any agent which by hydrolysis increases the amount of the free acid in solution tends to increase the efficiency of that solution.

[15] *T.*, 1912, **101**, 444. [16] *Ibid.*, 222.

Willard[17] has prepared pure perchloric acid dihydrate, $HClO_4,2H_2O$, from ammonium perchlorate by oxidation of the ammonia with aqua regia. The acid has the advantage of being very cheaply prepared in the pure state. It is not poisonous or explosive. As a rule it is non-oxidising except at the boiling point (203°). It will completely displace hydrofluoric, nitric, hydrochloric, or any other volatile acid, owing to its high boiling point. Its salts are soluble in water, alcohol, or acetone, and are very suitable for electrochemical work as they are not reduced. Its principal use is for the separation of sodium and potassium. Furthermore, it serves as an excellent standard solution in acidimetry, and it may be used in place of sulphuric acid in potassium permanganate titrations.

Group VIII.

Hantzsch[18] has put forward a suggestion regarding the constitution of the blue and red cobalt hydroxides. It is generally thought that the blue compound is a basic salt, for when it is precipitated from the sulphate by alkali and washed with cold water until no more sulphuric acid comes out it still contains SO_4.

Hantzsch states that this may be removed by repeated boiling with air-free water, without the colour being impaired. The red hydroxide is obtained by precipitating with excess of alkali, and washing the precipitate with hot water in an atmosphere of hydrogen, and giving it a final washing with alcohol and ether. It still retains some water after prolonged heating in an atmosphere of nitrogen at 300°, whilst the blue compound is completely dehydrated at 170°. Acetyl chloride and benzoyl chloride react more vigorously with the red compound than with the blue. Hantzsch calls this a case of chromoisomerism, and he suggests the formula $Co(OH)_2$ and $CoO \ldots H_2O$ for the red and blue compounds respectively.

Recoura[19] discusses the constitution of ferric sulphate trihydrate and ferric fluoride hexahydrate. If ferric sulphate hexahydrate is dehydrated at 108° it loses three molecules of water, and is converted into the yellow $Fe_2(SO_4)_3,3H_2O$. This substance when dissolved in alcohol gives no precipitate with barium chloride. The alcoholate, $Fe_2(SO_4)_3,2H_2O,2C_2H_6O$, previously described,[20]

[17] *J. Amer. Chem. Soc.*, 1912, **34**, 1480 ; *A.*, ii, 1163.

[18] *Zeitsch. anorg. Chem.*, 1912, **73**, 304 ; *A.*, ii, 166.

[19] *Compt. rend.*, 1911, **153**, 1223 ; 1912, **154**, 655 ; *A.*, ii, 165, 353 ; *Bull. Soc. chim.*, 1912, [iv], **11**, 370, 941.

[20] *Ann. Chim. Phys.*, 1907, [viii], **9**, 263 ; *Compt. rend.*, 1907, **144**, 1427 ; *A.*, 1907, ii, 552, 693.

loses half of its water at 105° without changing its appearance, whilst the remainder is lost together with the alcohol at 115°, the material becoming temporarily black. The alcohol molecules do not appear to be attached to the sulphuric acid as they are removed on solution in water, unlike the case of ethyl ferrisulphate. Recoura suggests for the trihydrate the formula $Fe_2(SO_3)_3(OH)_6$, similar to that of the green pentahydrate of chromic sulphate. He considers that the formula of ferric fluoride hexahydrate should be written $Fe_2F_4(OH)_2,(HF)_2,4H_2O$, and for this he advances the following reasons. Only a third of the iron reacts with barium fluoride, although the phenomenon is complicated by the precipitation of the double salt, $Fe_2F_6,3BaF_2$. When the solid salt is boiled with alcohol only one-third of the fluorine is rapidly eliminated as hydrogen fluoride, the remainder being lost very slowly. When heated to 95° the salt loses water rapidly and proportionally to the loss of fluorine, until one-third of the latter has been eliminated, after which no more water is lost.

E. C. C. Baly.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

A careful survey of the research work in the Aliphatic Division of Organic Chemistry done during the past year shows that practically all the investigations have been carried out along more or less well-known lines, and that no strikingly original discovery has been made. The work nevertheless represents a steady advance in this section of Organic Chemistry.

Hydrocarbons.

Pring and Fairlie[1] find that at a temperature of 1200° and at pressures from 10 to 60 cm. carbon and hydrogen unite to give, not only methane, but also ethylene, the rate of formation of the latter being about 1/100th that of the former. The rate of formation of ethylene increases with rise of temperature, and at 1400° the amount of this gas is comparable with that of the methane. The amount of acetylene formed at 1650° was sufficient to enable its presence to be experimentally demonstrated, but at 1200° the amount was insufficient for this purpose.

In a later communication[2] it is shown that the rate of formation of methane from its elements proceeds with increased velocity at high pressures, the equilibrium stage being reached in two hours, when the temperature was 1200—1300° and the pressure 30 to 50 atmospheres. The relative amount of methane produced increased with the pressure to the extent demanded by the law of mass action as applied to the equation $C+2H_2=CH_4$. Methane is the only saturated hydrocarbon formed at any temperature between 1100° and 2100° or pressure up to 200 atmospheres. It is probable that by using finely divided carbon and working at high pressures the direct union of carbon and hydrogen would be sufficiently rapid to enable this method to be used for the preparation of methane on a large scale.

[1] *T.*, 1911, **99**, 1796; *Ann. Report*, 1910, 102.

[2] *Ibid.*, 1912, **101**, 91.

Hauser and Herzfeld[3] find that ozonised oxygen reacts at the ordinary temperature with methane to produce formaldehyde, $CH_4 + 2O_3 = CH_2O + H_2O + 2O_2$, and that the reaction is practically quantitative even for low concentrations of the reacting substances. Since methane is the only hydrocarbon which is in this manner directly oxidised to formaldehyde, the reaction may with advantage be used for the detection of this gas. This action of ozone on methane affords an explanation of Gréhant's observation[4] that methane fires much more easily with oxygen obtained by electrolysis than with ordinary oxygen.

A study[5] of the action of acetylene and of substituted acetylenes on cuprous chloride shows that the initial product of the action is the compound $C_2H_2,CuCl$, or $C_2HR,CuCl$. Hence the equation $CR{:}CH + CuCl = CR{:}CCu + HCl$ fails to show that the formation of an additive compound of the reacting substances is the first phase of the reaction, and precedes substitution.

Berthelot's experiments on the pyrogenic condensation of acetylene have been repeated[6] on a large scale and under carefully controlled conditions. The acetylene was diluted with an equal volume of hydrogen in order to minimise its decomposition into methane and hydrogen, and the mixed gases passed through two electrically-heated tubes, the first of these being maintained at 640—650°, and the second at 800°. The resulting tar was of a light brown colour, had an aromatic odour, and in one experiment amounted to 63 per cent. of the weight of the acetylene used; the gases leaving the apparatus contained a considerable amount of methane. The tube heated at the lower temperature gave a tar rich in light oil, whereas that obtained from the other tube contained more of the hydrocarbons of high molecular weight. The following hydrocarbons were obtained from the tar by fractional distillation: benzene, toluene, diphenyl, naphthalene, anthracene, indene, fluorene, pyrene, and chrysene, the first-named forming about one-fifth of the whole tar. No styrene could be found, and the substance which Berthelot isolated and regarded as styrene was in all probability indene, the properties of these two substances being very similar. The low percentage of acetylene in ordinary coal gas is regarded as due to its decomposition into methane and carbon, and also to its condensation to cyclic hydrocarbons; in fact, the formation of the latter during the manufacture of coal gas is in a large measure due to this condensation, although it is true that

[3] *Ber.*, 1912, **45**, 3515; *A.*, 1913, ii, 77.

[4] *Compt. rend.*, 1907, **145**, 625; *A.*, 1907, ii, 990.

[5] W. Manchot, J. C. Withers, and H. C. Oltrogge, *Annalen*, 1912, **387**, 257; *A.*, i, 230.

[6] R. Meyer, *Ber.*, 1912, **45**, 1609; *A.*, i, 525.

Pictet and Ramseyer[7] have isolated hexahydrofluorene from coal itself.

The compound $5Na_2S_2O_3,5Cu_2S_2O_3,5Cu_2C_2,C_2H_2,10H_2O$ is obtained as a red precipitate by passing acetylene into a solution of sodium thiosulphate and copper acetate.[8] It burns like gunpowder when heated, and dissolves in water, giving a red solution, the colour of which is destroyed by acids and restored by alkali only if the latter is added immediately after the removal of the colour by the acid.

Caoutchouc.—W. H. Perkin[9] has published an account of the work which he and several collaborators have carried out in the direction of the preparation of synthetic rubber by methods which may ultimately admit of commercial application. A careful consideration of the question showed that for a process to be a commercial success it must be capable of producing the rubber at 2s. 2d. per kilo. [1s. per lb.], or even less. This limits the choice of raw materials to substances such as wood, starch or sugar, petroleum, and coal, and of these, starchy substances would appear to hold out the most hope of success. These considerations led to experiments on fusel oil, and as a result a method was devised by which isoprene can be obtained readily and in quantity from *iso*amyl alcohol. Commercial fusel oil on distillation gives a fraction (b. p. 128—130°) which consists approximately of 87 per cent. of *iso*amyl alcohol and 13 per cent. of active amyl alcohol. This fraction was first converted into the chloride by the action of dry hydrogen chloride, and then chlorinated in a special apparatus designed for the purpose, and with the object of limiting as far as possible the chlorination to the formation of dichlorides. The resulting product on fractional distillation gave $\gamma\delta$-dichloro-β-methylbutane,

$$CHMe_2{\cdot}CHCl{\cdot}CH_2Cl,$$

$\beta\delta$-dichloro-β-methylbutane, $CClMe_2{\cdot}CH_2{\cdot}CH_2Cl$, and $\alpha\delta$-dichloro-β-methylbutane, $CH_2Cl{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Cl$. In subsequent experiments these isomerides were not separated, and the portion of the chlorinated product which boiled at 140—180° was passed over soda-lime at 470° and the resulting vapours condensed. The liquid thus obtained was fractionally distilled, and yielded isoprene in a 40 per cent. yield of that theoretically possible. The formation of isoprene from $\gamma\delta$-dichloro-β-methylbutane is no doubt due to a molecular rearrangement of the *iso*propylacetylene, $CHMe_2{\cdot}C{\equiv}CH$, which is first formed. In order to polymerise the isoprene to rubber it was sealed up in tubes with about 3 per cent. of thin sodium

[7] *Ber.*, 1911, **44**, 2486; *A.*, 1911, i, 850; also Burgess and Wheeler, *T.*, 1911, **99**, 649.

[8] K. Bhaduri, *Zeitsch. anorg. Chem.*, 1912, **76**, 419; *A.*, i, 597.

[9] *J. Soc. Chem. Ind.*, 1912, **31**, 616; *A.*, i, 636.

wire (Matthews' sodium process), and heated for several days at about 60°; the dark brown product was then treated with acetone, and the precipitated rubber washed with alcohol or treated with steam to remove acetone and any unpolymerised hydrocarbon. Metallic sodium is a very effective agent for the polymerisation of such hydrocarbons as isoprene, butadiene, etc., as its action is practically quantitative, and is not seriously affected by the presence of other hydrocarbons which do not polymerise to rubber.

Perhaps the greatest difficulty which the above process offers to its being employed on a manufacturing scale is the limited supply of fusel oil, and in order to overcome this difficulty Fernbach[10] worked out fermentation processes by which, not only this substance, but also acetone can be obtained much more cheaply. Moreover, the fusel oil obtained by Fernbach's method contains a large proportion of butyl alcohol, from which butadiene is readily obtained by submitting it to a process similar to that employed for the preparation of isoprene from *iso*amyl alcohol. The resulting $\Delta^{\alpha\gamma}$-butadiene on treatment with sodium yields a rubber of better quality than that obtained from isoprene.[11]

In the third method worked out, acetaldehyde was treated with very dilute potassium carbonate, and the resulting aldol reduced by neutral reducing agents or electrolytically, when $\alpha\gamma$-butylene glycol was obtained. This glycol on treatment with hydrogen chloride gave the corresponding dichlorobutane, from which butadiene was obtained by the soda-lime method.

The product obtained by the polymerisation of vinyl bromide, and known as caouprene bromide,[12] exists in three modifications, $\alpha \rightarrow \beta \rightarrow \gamma$, which are capable of change in the direction indicated when submitted to the action of ultraviolet light or boiled with anhydrous acetic acid. Harries' butadiene-caoutchouc bromide,[13] which also exists in three modifications, is either identical or isomeric with caouprene bromide, the isomerism being due to a difference in the distribution of the bromine in the molecule. The constitution of caouprene bromide is most probably expressed by the formula:

$$\begin{array}{l} CH_2\text{--}CHBr\text{--}CH_2\text{--}CHBr\text{--}CH_2\text{--}CHBr \\ CHBr\cdot CH_2\cdot CHBr\cdot CH_2\cdots\cdots CH_2\cdot CHBr \end{array}$$

in which the dotted lines represent an unknown number of $\cdot CH_2\cdot CHBr\cdot$ groups.

Both caouprene bromide and butadiene-caoutchouc bromide yield

[10] *Eng. Pat.* 15,203, June 29, 1911; *ibid.*, 16,925, July 24, 1911.
[11] Harries, *Annalen*, 1911, **383**, 157; *A.*, 1911, i, 798; *Ann. Report*, 1911, 108.
[12] I. Ostromisslensky, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 204; *A.*, i, 280.
[13] *Annalen*, 1911, **383**, 157; *A.*, 1911, i, 798.

the same caoutchouc when treated with zinc dust, this reaction completing a new synthesis of butadiene-caoutchouc:

$$CH_2{:}CHBr \longrightarrow \text{caouprene bromide} \xrightarrow{Zn} \text{butadiene-caoutchouc.}$$

A large number of processes have been worked out for the preparation of unsaturated hydrocarbons like isoprene, butadiene, etc., which admit of polymerisation to caoutchouc-like substances, and in the majority of cases these have been patented. No useful purpose would be served by the publication in this report of all these various processes, because unless they eventually admit of commercial application the great majority of them are of little interest.

Caoutchouc when treated with ozone free from oxozone gives the true diozonide, $C_{10}H_{16}O_6$, whereas crude ozone gives the dioxozonide, $C_{10}H_{16}O_8$, which is more soluble than the true diozonide.[14] Both ozonides on hydrolysis give lævulinaldehyde and lævulic acid, in the proportion of 4 to 3 in the case of the diozonide, and 2·8 to 4 for the dioxozonide. Synthetic rubber gives results similar to those obtained with natural caoutchouc.

Spence[15] and his collaborators have continued their investigation on the vulcanisation of caoutchouc. They regard as "free" sulphur that portion of this element which is extracted from vulcanised caoutchouc by acetone or hot sodium hydroxide solution, the undissolved portion being the "fixed" sulphur. From the results of their experiments they conclude that it is possible to vulcanise caoutchouc so that no "free" sulphur is present in the product, the process under these conditions being essentially a chemical one with the formation of a product which in composition agrees closely with that required by the formula $C_{10}H_{16}S_2$; this view that vulcanisation is a chemical process is in direct opposition to the adsorption theory. With regard to the "free" sulphur present in vulcanised caoutchouc part only is adsorbed, the remainder being in the non-adsorbed condition. With good specimens of caoutchouc there is practically no vulcanisation at 40°, and only very little at 60°, but above this temperature it increases rapidly. On the other hand, partly decomposed caoutchouc undergoes considerable vulcanisation at 40°.

Bary and Weydert[16] are of opinion that the reaction of vulcanisation of caoutchouc is a reversible one, but the numerical data obtained are not in agreement with the law of mass action, whatever hypothesis may be adopted as to the degree

[14] C. Harries, *Ber.*, 1912, **45**, 936; *A.*, i, 407.

[15] D. Spence, *Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 304; **9**, 83, 300; 1912, **10**, 299; **11**, 28; *A.*, 1911, i, 657, 801; 1912, i, 123, 638, 706.

[16] *Compt. rend.*, 1911, **153**, 676; *A.*, 1911, i, 1003.

of polymerisation of the hydrocarbon. In the process of vulcanisation the sulphur first becomes attached to the terminal double linkings of a chain, and any further vulcanisation can only occur after depolymerisation. Bary[17] has obtained an approximate value for the molecular weight of caoutchouc; thus, when sulphur is added to caoutchouc in quantity insufficient for vulcanisation of the whole of the caoutchouc, and the mixture suitably heated, the resulting product consists of the sulphide $(C_{10}H_{16})_nS_2$ and caoutchouc; the former is insoluble in cold benzene, whereas the latter dissolves in this solvent. By gradually increasing the proportion of sulphur in successive experiments a point is reached at which there is just sufficient sulphur to convert the whole of the caoutchouc into the compound $(C_{10}H_{16})_nS_2$; in these circumstances the whole of the product is insoluble in benzene. Analysis of the compound thus produced shows that it contains 2·5 per cent. of sulphur, from which $n=\frac{97\cdot5\times32\times2}{2\cdot5\times136}=18\cdot4$. This value of n is in fair agreement with Weber's formula, $C_{200}H_{320}S_2$, and it would thus appear that the molecular weight of caoutchouc at the temperature of vulcanisation (140°) is approximately 2720.

Beadle and Stevens[18] have shown that the nitrogenous substance present in Para rubber plays an important part in the process of vulcanisation. Natural rubber from which this protein has been removed vulcanises less readily, and combines with less sulphur than the same specimen in which the protein is present. Although the protein-free rubber is much more distensible than the other, yet its tensile strength is much less. The absence of protein from synthetic rubber no doubt renders it inferior to the natural product; even if a protein is added to the synthetic rubber it is very unlikely that it will be possible to give it the reticulated structure so characteristic of the protein in the natural product.

In a lecture delivered before the Verein Deutscher Chemiker at Freiburg in Breisgau, Harries dealt with synthetic caoutchouc from the scientific point of view, and in a second lecture by Hofmann the same subject was treated from the technical side.[19]

A series of articles by I. L. Kondakoff on "Synthetic Rubber, its Homologues and Analogues," have appeared during the current year in the *Revue Générale de Chimie*.

[17] *Compt. rend.*, 1912, **154**, 1159; *A.*, i, 481.

[18] *Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 61; *A.*, i, 789; *India-rubber Journ.*, 1912, **44**, 554; *J. Soc. Chem. Ind.*, 1912, **31**, 1099.

[19] *Zeitsch. angew. Chem.*, 1912, **25**, 1457, 1462; *A.*, i, 706.

Alcohols and Aldehydes.

The action of dry potassium hydroxide on various alcohols has been studied by Guerbet,[20] who finds that when a primary alcohol containing six or more carbon atoms is heated at 230° with potassium hydroxide it is oxidised to the corresponding acid, the yield being almost quantitative; with a lower primary alcohol the yield of acid is less, because a considerable amount of unsaturated hydrocarbon is formed. When a secondary alcohol is submitted to a similar treatment very little is oxidised, the greater portion condensing to higher alcohols, thus: *iso*propyl alcohol gives β-methylpentan-δ-ol, $CHMe_2 \cdot CH_2 \cdot CHMe \cdot OH$, and βδ-dimethylheptan-γ-ol, $CHMe_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CHMe \cdot OH$. Tertiary alcohols are scarcely attacked by potassium hydroxide at 230°, but above this temperature they are slowly oxidised to acids containing fewer carbon atoms. The above reaction is suggested as a simple method for distinguishing between primary, secondary, and tertiary alcohols.

Senderens[21] has published a full résumé of the work done by himself and others on the catalytic dehydration of alcohols by various elements, oxides, and salts; the comparative efficiency of several catalysts being given in a tabular form. The mechanism of the reaction is discussed, and the view favoured is that a compound of the catalyst and the alcohol is first formed, and that this subsequently decomposes. In view of the fact that the majority of the work has already been dealt with in previous reports,[22] this short notice of the present publication will be sufficient.

The formation of unsaturated hydrocarbons from alcohols by means of sulphuric acid has been shown to be greatly facilitated by the presence of such a catalyst as anhydrous aluminium sulphate,[23] and the results of an inquiry as to whether the sulphuric acid itself acts as a true catalyst or merely in virtue of its power to absorb water, point to the former alternative being the correct one.[24] For every catalytic action there is a definite temperature, below which the effect of the catalyst does not come into play. For tertiary aliphatic alcohols and sulphuric acid this temperature is below the boiling point of the lowest member of the series; for secondary alcohols it is below the boiling point of the C_5 member; and in the case of the primary alcohols it is near that of the C_8 member; hence all tertiary alcohols, secondary alcohols above the

[20] *Compt. rend.*, 1911, **153**, 1487; 1912, **154**, 222, 713; *A.*, i, 67, 154, 331.

[21] J. B. Senderens, *Ann. Chim. Phys.*, 1912, [viii], **25**, 449; *A.*, i, 406.

[22] *Ann Report*, 1907, 75; 1908, 77; 1909, 76; 1910, 99.

[23] J. B. Senderens, *Compt. rend.*, 1910, **151**, 392; *A.*, i, 649; *Ann. Report*, 1910, 100; J. B. Senderens and J. Aboulenc, *Compt. rend.*, 1911, **152**, 1671; *A.*, i, 600.

[24] J. B. Senderens, *ibid.*, 1912, **154**, 777; *A.*, i, 331.

C_5 member, and primary alcohols above the C_8 member readily yield the corresponding unsaturated hydrocarbon when boiled with 3 to 4 per cent. of their volume of sulphuric acid. In the case of the lower alcohols, as, for instance, ethyl alcohol, by using a large excess of sulphuric acid the alcohol is prevented from boiling away before the temperature at which catalytic action takes place is reached.

The dehydration of alcohols can also be effected by the use of toluene-*p*-sulphonic acid[25]; thus *tert.*-butyl alcohol is readily converted into *iso*butylene by heating with 1·7 to 5 per cent. of its weight of the sulphonic acid.

Senderens[26] has shown that ketones are readily prepared by passing the vapour of an acid or a mixture of two acids over thorium oxide heated at 380—400°, and the principle of this method has now been extended to the preparation of aldehydes.[27] For this purpose a mixture of the acid and excess of formic acid is passed over titanium oxide at 250—300°. The formic acid is decomposed into carbon monoxide and water, and the carbon monoxide reduces the other acid to the corresponding aldehyde:

$$R\cdot CO_2H + H\cdot CO_2H = R\cdot CHO + CO_2 + H_2O.$$

The yield of aldehyde is quite satisfactory, varying from 50 per cent. in the case of acetic acid to 95 per cent. in the case of octoic acid.

Romijn's[28] method for the estimation of formaldehyde is based on the interaction of this substance and potassium cyanide, whereby the reaction $CH_2O + KCN = CN\cdot CH_2\cdot OK$ is supposed to take place. Kohn[29] obtained potassium glycollate and hexamethylenetetramine as products of the interaction of these two substances when an excess of formaldehyde was used. The action of potassium cyanide on formaldehyde has been recently reinvestigated by Polstorff and Meyer,[30] who have identified ammonia, glycollic acid, iminodiacetic acid, and nitrilotriacetic acid as products of the interaction when a 25 per cent. aqueous solution of potassium cyanide and one of about 18 per cent. of formaldehyde are mixed at 0°, and the mixture kept at the ordinary temperature for twenty-four hours. The following equations represent the changes which take place:

[25] H. Wuyts, *Bull. Soc. chim. Belg.*, 1912, **26**, 304 ; *A.*, i, 598.

[26] J. B. Senderens, *Compt. rend.*, 1908, **146**, 1211 ; 1909, **148**, 927 ; **149**, 213, 995 1910, **150**, 111, 702, 1336 ; *A.*, 1908, i, 494 ; 1909, i, 286, 627 ; 1910, i, 11, 179, 318, 489.

[27] P. Sabatier and A. Mailhe, *ibid.*, 1912, **154**, 561 ; *A.*, i, 238.

[28] *Zeitsch. anal. Chem.*, 1897, **36**, 18 ; *A.*, 1897, ii, 166.

[29] *Monatsh.*, 1899, **20**, 903 ; *A.*, 1900, i, 205.

[30] *Ber.*, 1912, **45**, 1905 ; *A.*, i, 605 ; see also H. Franzen, *J. pr. Chem.* 1912, [ii], **86**, 133 ; *A.*, i, 677.

$KCN + CH_2O = CN\cdot CH_2\cdot OK.$

$CN\cdot CH_2\cdot OH + 2H_2O = CO_2H\cdot CH_2\cdot OH + NH_3.$

$CN\cdot CH_2\cdot OH + NH_3 = CN\cdot CH_2\cdot NH_2 + H_2O.$

$NH_2\cdot CH_2\cdot CN + HO\cdot CH_2\cdot CN \longrightarrow NH(CH_2\cdot CN)_2 \longrightarrow NH(CH_2\cdot CO_2H)_2.$

$NH_2\cdot CH_2\cdot CN + 2HO\cdot CH_2\cdot CN \longrightarrow N(CH_2\cdot CN)_3 \longrightarrow N(CH_2\cdot CO_2H)_3.$

A good yield of glycollic acid can be obtained by distilling with steam the mixture of potassium cyanide and formaldehyde five to ten minutes after mixing.

An attempt [31] to determine the composition of the resin produced by the action of dilute alkali on acetaldehyde at low temperatures has resulted in the separation of the resin into two isomerides, $C_{24}H_{36}O_6$; these have been converted into chloro- and bromo-derivatives, but the form in which the oxygen is present has not yet been determined.

Substances like acraldehyde which readily polymerise have recently become of special interest in view of the preparation of baekelite and synthetic caoutchouc. In the elimination of the elements of water from glycerol the hydroxyl group may come from a primary or secondary alcoholic group, and the changes which takes place may be formulated thus:

$$\begin{array}{l} [OH\cdot CH_2\cdot C(OH){:}CH_2] \longleftrightarrow OH\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow \\ \qquad\uparrow \qquad\qquad\qquad\qquad\qquad\qquad CH_2O + CH_3\cdot CHO \quad (I) \\ OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH \\ \qquad\downarrow \\ [OH\cdot CH_2\cdot CH{:}CH\cdot OH] \longleftrightarrow OH\cdot CH_2\cdot CH_2\cdot CHO \longrightarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad CH_2{:}CH\cdot CHO \quad (II) \end{array}$$

Secondary alcoholic groups are dehydrated more readily than primary ones, and so in accordance with the above schemes the production of acraldehyde should be facilitated by the dehydration of the glycerol at a low temperature. Potassium hydrogen sulphate and the sulphates of aluminium, copper, and iron are suitable for the dehydration, but unfortunately the acraldehyde contains a considerable amount of sulphur dioxide; on the other hand, the sulphates of the alkaline earths and of the heavy metals yield an acraldehyde free from this impurity. Granular dehydrated magnesium sulphate gives the best results, and by heating the glycerol with this substance at 330—340° and in a special apparatus, a yield of 60 per cent. of acraldehyde is obtained,[32] as much as one kilogram having been prepared in one day. If the temperature is appreciably (30°) higher than the one quoted then the acralde-

[31] T. Ekecrantz, *Arkiv. Kem. Min. Geol.*, 1912, **4**, No. 27; *A.*, i, 778.

[32] A. Wohl and B. Mylo, *Ber.*, 1912, **45**, 2046; *A.*, i, 677.

hyde contains a considerable amount of acetaldehyde formed in accordance with scheme I.

The preparation of aliphatic dialdehydes is always a matter of considerable difficulty on account of the ease with which they polymerise; this difficulty is greatly increased when the dialdehyde to be prepared is also a hydroxy-compound, for hydroxy-aldehydes are very sensitive to acids and alkalis. Wohl and Mylo,[33] by their preparation of tartardialdehyde, have successfully overcome the difficulties associated with the preparation of a substance of this type:

$$EtMgBr + C_2H_2 \longrightarrow BrMgC{:}CMgBr \xrightarrow{2CH(OEt)_3} (EtO)_2CH\cdot C{:}C\cdot CH(OEt)_2$$

$$(EtO)_2CH\cdot C(H){:}C\cdot CH(OEt)_2 \xleftarrow{+\text{colloidal platinum}} (EtO)_2CH\cdot CH{:}CH\cdot CH(OEt)_2 \quad (A.)$$

$$(EtO)_2CH\cdot CH(OH)\cdot CH(OH)\cdot CH(OEt)_2 \xrightarrow{KMnO_4}$$

$$CHO\cdot CH(OH)\cdot CH(OH)\cdot CHO \xleftarrow{\text{dilute acids}}$$

The unimolecular form of tartardialdehyde was obtained in aqueous solution only; this had a sweet taste, and on slow evaporation deposited needles which were sparingly soluble, and no doubt represented a polymeric form of the aldehyde. The needles had a bitter taste, and dissolved slowly in warm water, giving a sweet solution, in which the aldehyde was present in a unimolecular form, as shown by cryoscopic measurements. When oxidised with bromine water the dialdehyde gives mesotartaric acid, a result which indicates that the ethylenic acetal (A) has a *cis*-configuration.

By the hydrolysis of the diacetal,

$$(EtO_2)_2CH\cdot CH{:}CH\cdot CH(OEt)_2,$$

with very dilute sulphuric acid, the same authors [34] have obtained maleic dialdehyde. This substance has a bitter, burning taste, and a strong, pungent odour not unlike acrolein or formaldehyde, but perhaps its most remarkable property is its yellow colour, which is even deeper than that of diacetyl. This depth of colour is remarkable in a compound with such a low molecular weight, and is, no doubt, due to the accumulation of double linkings; and regarded from this point of view the formulæ of maleic dialdehyde and *p*-benzoquinone are seen to be very similar:

$$O{:}C\langle \begin{matrix} CH{:}CH \\ H \quad\quad H \end{matrix} \rangle C{:}O \qquad\qquad C{:}O\langle \begin{matrix} CH{:}CH \\ CH{:}CH \end{matrix} \rangle C{:}O.$$

Acids, Acid Chlorides, and Esters.

The evidence in support of the view that addition precedes substitution in organic compounds, especially those containing a carbonyl group, is gradually becoming more conclusive. Lapworth,[35]

[33] *Ber.*, 1912, **45**, 322; *A.*, i, 161. [34] *Ibid.*, 1746. [35] *T.*, 1904, **85**, 30.

some years ago, brought forward evidence in support of it by his investigation of the action of bromine on acetone, and further evidence in the same direction is supplied by the work of Dawson, Miss Leslie, and Powis [36] on the reaction between acetone and iodine, the results obtained leading these observers to the conclusion that the reaction takes place in three stages:

$$CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2{:}C(OH){\cdot}CH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$CH_2{:}C(OH){\cdot}CH_3 + I_2 \longrightarrow CH_2I{\cdot}CI(OH){\cdot}CH_3 \quad . \quad . \quad . \quad (2)$$
$$CH_2I{\cdot}CI(OH){\cdot}CH_3 \longrightarrow CH_2I{\cdot}CO{\cdot}CH_3 + HI \quad . \quad . \quad . \quad . \quad (3)$$

changes (2) and (3) being of relatively high speed in comparison with the primary isomeric change (1).

The mechanism of the reaction for the preparation of α-bromo-acids by the Hell-Volhard method is probably of the same nature, and may be formulated thus:

$$R{\cdot}CH_2{\cdot}COCl \longrightarrow R{\cdot}CH{:}C\begin{matrix}OH\\Cl\end{matrix} \xrightarrow{Br_2}$$

$$R{\cdot}CHBr{\cdot}C\begin{matrix}Br\\OH\\Cl\end{matrix} \longrightarrow \begin{matrix}R{\cdot}CHBr{\cdot}COCl + HBr.\\R{\cdot}CHBr{\cdot}COBr + HCl.\end{matrix}$$

Evidence in support of the above scheme is furnished by Aschan,[37] who shows that the product of the action of bromine on various acid chlorides is a mixture of the brominated acid bromide and brominated acid chloride, in which the former predominates. A very similar result has been obtained by Smith and Lewcock [38] in their investigation of the action of bromine on *iso*butyryl chloride; in this case the brominated product consisted almost entirely of α-bromo*iso*butyryl bromide. The evidence brought forward by Meyer,[39] although leading to the same conclusions, is based on entirely different considerations. Meyer points out that, according to Lapworth, if the process is one of direct substitution, then the reaction must be a bimolecular one, and its velocity must depend on the concentration of both the acid and the bromine. On the other hand, if enolisation first occurs (slowly) and is then followed by addition (rapid) of bromine, etc., then the reaction is unimolecular, and its velocity is independent of the concentration of the bromine. Experiments on the action of bromine on malonic acid show that the velocity of the reaction is quite independent of the concentration of the bromine. Meyer also points out that the formation of the brominated acid bromide in the experiments of Aschan may equally well be explained by the theory of direct substitution; in

[36] *T.*, 1909, **95**, 1864; 1912, **101**, 1503.
[37] *Ber.*, 1912, **45**, 1913; *A.*, i, 599.
[38] *Ibid.*, 2358; *A.*, i, 826.
[39] *Ibid.*, 2864; *A.*, i, 941.

this case the hydrogen bromide set free reacts with the brominated acid chloride:

$$CH_3\cdot COCl \xrightarrow{Br_2} CH_2Br\cdot COCl + HBr = CH_2Br\cdot COBr + HCl,$$

just as potassium bromide reacts with acetyl chloride to give acetyl bromide and potassium chloride. Similar criticism can be applied to the results obtained by Smith and Lewcock.

Two new isomerides[40] of oleic acid have been prepared from ricinoleic acid as a starting point. When this acid is reduced by hydrogen in presence of platinous hydroxide it gives λ-hydroxystearic acid; this latter acid when heated with hydrobromic acid yields a bromostearic acid, which by treatment with alcoholic potassium hydroxide gives a solid and a liquid product. From the solid product one of the isomerides was isolated and identified as Δ^{λ}-oleic acid (m. p. 34—36°). The liquid product contained the other isomeride, which from its reactions is in all probability Δ^{κ}-oleic acid.

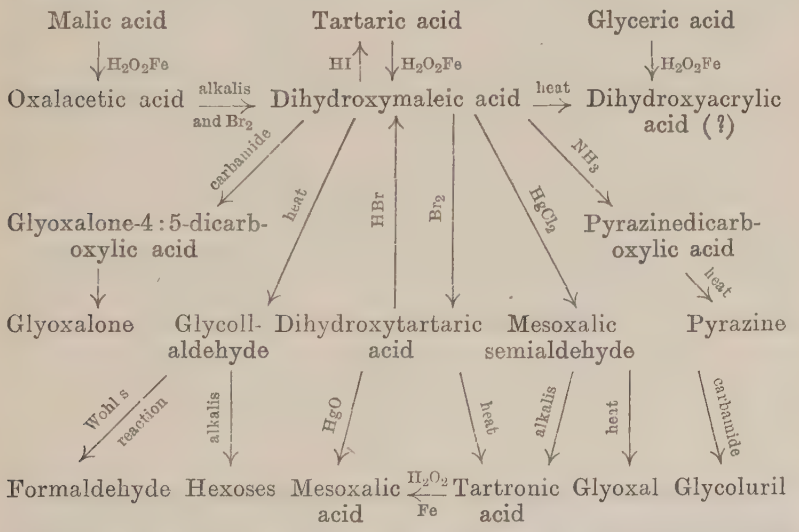
The rate of absorption of halogens by unsaturated acids is undoubtedly dependent in some measure on the relative position of the double bond and the carboxyl group; ordinary oleic acid, for instance, readily absorbs bromine, whereas the absorption of this element by Δ^{β}-oleic acid is very slow. Further evidence in support of this has been obtained[41] by the determination of the iodine values for undecenoic, crotonic, Δ^{β}-hypogæic, and Δ^{β}-oleic acids; thus with Δ^{β}-oleic acid the following iodine values were obtained: 18·0 after thirty minutes, 37·7 after three hours, 76·2 after twelve hours, 84·2 after twenty-four hours, and 86·8 after seventy hours, the theoretical value being 89·7. It is suggested that the determination of the iodine value may help in locating the position of the double bond in an unsaturated acid.

Fenton and Jones[42] obtained oxalacetic acid (m. p. 180—184°) by the oxidation of malic acid with hydrogen peroxide in the presence of ferrous iron, the acid being isolated from the reaction mixture by the addition of sulphuric acid and extraction with ether. Wohl and Oesterlin[43] shortly afterwards obtained by a different method an acid having the composition and properties of oxalacetic acid, but melting at 152°; it was shown later that the new acid when dissolved in sulphuric acid and extracted with ether is converted into the acid melting at 184°. From a comparison of their physical and chemical properties it was concluded that the two acids are geometrical isomerides, and that the acid melting

[40] S. Fokin, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 653; *A.*, i, 534.
[41] G. Ponzio and C. Gastaldi, *Gazzetta*, 1912, **42**, ii, 92; *A.*, i, 748.
[42] *T.*, 1900, **77**, 77.
[43] *Ber.*, 1901, **34**, 1139; *A.*, 1901, i, 365.

at 184° is hydroxyfumaric acid, the other being hydroxymaleic acid. When tartaric acid is oxidised in the presence of ferrous iron an acid, $C_4H_4O_6,2H_2O$, is obtained, which, from its readiness to form an anhydride, etc., is regarded as dihydroxymaleic acid.[44] Fenton and Wilks[45] now show that the "oxalacetic acid" melting at 184° can be directly transformed into "dihydroxymaleic acid," and point out that from this result it would appear that if "the spacial relations of the original molecule persist in the new product," then the "oxalacetic acid" melting at 184° and "dihydroxymaleic acid" must have the same geometrical configuration; in other words, this is evidence in favour of ascribing the fumaroid configuration to "dihydroxymaleic acid." This evidence cannot, however, be regarded as conclusive, for the result can be explained in other ways.

The subjoined scheme summarises the various transformations which have been accomplished with these acids and other allied compounds:



During the last two years J. F. Thorpe[46] and his collaborators have published six important papers dealing with the constitution of glutaconic acid and its derivatives. Glutaconic acid is known in one form only, although the formula generally assigned to it, $CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$, requires the existence of *cis-* and *trans-*

[44] H. J. H. Fenton, *T.*, 1905, **87**, 804.

[45] *T.*, 1912, **101**, 1570.

[46] F. B. Thole and J. F. Thorpe, *ibid.*, 1911, **99**, 2187, 2208; N. Bland and J. F. Thorpe, *ibid.*, 1912, **101**, 856, 871, 1557, 1739; *Ann. Report*, 1905, 91; 1910, 89.

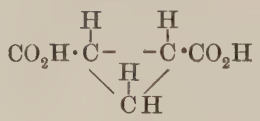
modifications, but all attempts to obtain these have failed. Further, it has been shown that the α-alkylglutaconic acids,

$$CO_2H\cdot CHR\cdot CH{:}CH\cdot CO_2H,$$

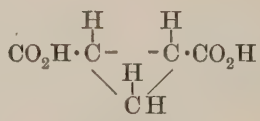
and γ-alkylglutaconic acids, $CO_2H\cdot CH_2\cdot CH{:}CR\cdot CO_2H$, are the same substances; also, that α-methyl-γ-ethylglutaconic acid,

$$CO_2H\cdot CHMe\cdot CH{:}CEt\cdot CO_2H,$$

and γ-methyl-α-ethylglutaconic acid, $CO_2H\cdot CHEt\cdot CH{:}CMe\cdot CO_2H$, are identical. To explain these facts, it has been suggested that the constitution of glutaconic acid is best represented by the formula $CO_2H\cdot CH\cdot CH[H]\cdot CH\cdot CO_2H$, the hydrogen atom within the bracket being regarded as a mobile atom in equilibrium between the two neighbouring carbon atoms. An acid containing such a mobile hydrogen atom is termed a mobile acid, and it is assumed that for every mobile acid there is a static stable state called the normal state, in which the tautomeric hydrogen atom is attached to the central carbon atom of the three-carbon system. Such an acid is called a normal acid, and its structure is similar to that of *iso*phthalic acid.

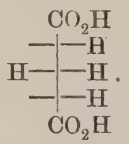


Glutaconic acid.



*iso*Phthalic acid.

Although the manner in which the free valencies of the two terminal carbon atoms of the three-carbon system are combined is left an open question, they are regarded as being on the same sides of the two terminal tetrahedrons, corresponding with the *meso*- or non-resolvable form, thus:

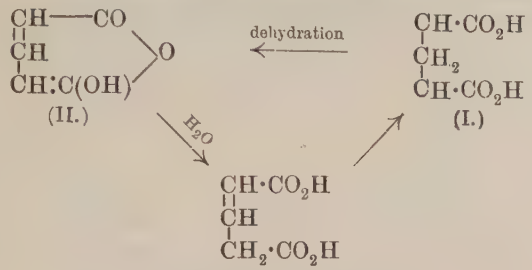


The normal acids are the so-called *trans*-modifications of the acids of this series.

Attempts to prepare an anhydride from a mobile acid by the action of acetyl chloride lead, not to an ordinary anhydride, but to an hydroxy-anhydride (II), which, on subsequent hydrolysis, yields, in the case of glutaconic acid itself, the normal form of the acid (I).

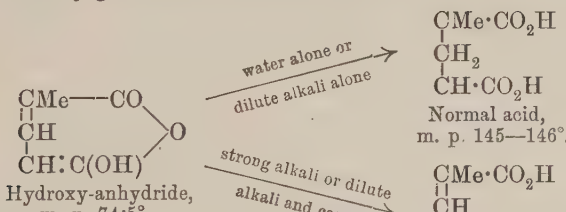
Now, if formula (II) correctly represents the constitution of the anhydride formed by the dehydration (by acetyl chloride) of the normal form of the acid, it is obvious that the first product of hydration of this anhydride must be the acid (III), called the

labile acid. In the case of glutaconic acid itself, only the normal form (I) is known, and the non-isolation of the labile form (III)



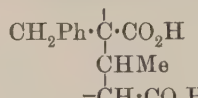
(III.) Labile acid
(unknown for glutaconic acid).

is accounted for by the supposition that at the moment of its formation from the hydroxy-anhydride, the initial momentum of the entering hydrogen atom is sufficient to carry it at once into the three-carbon system. If, however, the initial momentum is decreased by the introduction of an alkyl group on one of the carbon atoms, it is possible to cause the hydrogen atom to remain within the carbonyl system by effecting the hydration of the hydroxy-anhydride by strong alkali or dilute alkali in the presence of casein. If, however, the hydrolysis is brought about by water alone or dilute alkali without casein, then the normal acid results. Thus, for α-methylglutaconic acid, we have:

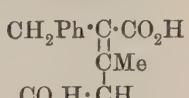


The labile acids are the so-called *cis*-forms of the acids of this series. It is evident that a labile acid should be capable of existing in *cis*- and *trans*-modifications, but in the case of the simpler members of the series the very unstable character of the labile acids causes them to pass into the stable normal form by all reactions which should give the fumaroid modification. The stability of a labile acid, however, is greatly increased by the presence of a heavy group attached to one of the terminal carbon atoms of the three-carbon system, more especially if a methyl group is also present attached to the central carbon atom of the system; in other words, the labile form of α-benzyl-β-methylglutaconic acid

might be sufficiently stable to admit of its isolation in both the *cis*- and *trans*-modifications. Bland and Thorpe[47] have consequently prepared this substance, and find that the labile acid which they obtain has the *trans*-configuration, and all attempts to get the corresponding *cis*-form have been unsuccessful:

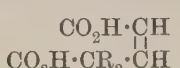


Normal acid, m. p. 148°.



trans-Labile acid, m. p. 134°.

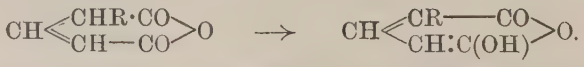
The fact therefore remains that up to the present no labile form of a glutaconic acid has been obtained in both *cis*- and *trans*-modifications. The reactions of substituted glutaconic acids of the type $CO_2H\cdot CR_2\cdot CH{:}CH\cdot CO_2H$, in which there is no mobile hydrogen atom, are normal in all respects, and the isomerism of these acids is of the ordinary *cis*- and *trans*-variety, thus:



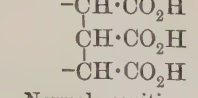
cis-form.

trans-form.

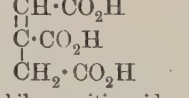
If the dehydration of the substituted glutaconic acid, say α-methylglutaconic acid, is effected by the use of phosphorus pentachloride[48] instead of acetyl chloride, then the anhydride produced is the ordinary anhydride, $CH\langle\begin{matrix}CHR\cdot CO\\CH-CO\end{matrix}\rangle O$; these ordinary anhydrides, when distilled, are converted into the hydroxyanhydrides:



Aconitic acid may be regarded as a β-substituted glutaconic acid, and it follows, from what has been said about the glutaconic acids, that aconitic acid should exist in the normal form (I) and the labile form (II); moreover, since it is a β-substituted acid, the stability of the labile form should be sufficient to admit of its isolation.[49]



Normal aconitic acid.
(I.)

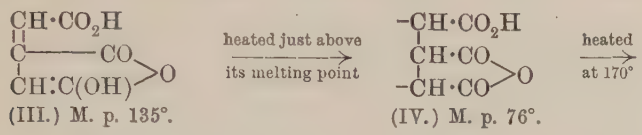


Labile aconitic acid.
(II.)

When aconitic acid is treated with ordinary acetyl chloride,

[47] *T.*, 1912, **101**, 1744.
[48] F. Feist and G. Pomme, *Annalen*, 1909, **370**, 61; *A.*, 1910, i, 9.
[49] N. Bland and J. F. Thorpe, *T.*, 1912, **101**, 1490.

which always contains phosphorus trichloride, it is converted into the normal anhydro-acid [50] (IV), melting at 76°, whereas if pure acetyl chloride be used, then the product is the hydroxy-anhydro-acid (III), melting at 135°. That formula III correctly represents the constitution of this latter substance is proved by the fact that it gives an intense coloration with ferric chloride, behaves as a dibasic acid, and on heating undergoes the following changes:



(III.) M. p. 135°. (IV.) M. p. 76°.

Itaconic anhydride. Citraconic anhydride.

When the normal anhydro-acid (IV) is treated with strong alkali or dilute alkali in the presence of casein, it gives the ordinary form (I) of aconitic acid (m. p. 191°), whereas the hydroxy-anhydro-acid (III), when similarly treated, gives the labile form (II) of aconitic acid, melting at 173°.

The labile acid is a comparatively stable substance, which, although exhibiting no points of difference from normal aconitic acid in respect of its salts, yet differs markedly from this acid in its behaviour on dehydration, since on treatment with pure or impure (containing phosphorus trichloride) acetyl chloride it is completely converted into the hydroxy-anhydro-acid. When boiled with dilute hydrochloric acid, the labile acid is slowly converted into the normal acid.

The reactivity [51] of the acid dichlorides of fumaric acid and its haloid derivatives is very much greater than that of the corresponding compounds of maleic acid. Thus, whereas all fumaroid dichlorides react almost instantaneously with aniline to form anilides, and with methyl alcohol to form esters, the interaction between malenoid dichlorides and bases or alcohols is very much slower, and in some cases requires days before it approaches completion. This low reactivity of the malenoid dichlorides cannot be due to the proximity of the two ·COCl-groups, for if this were so, then *s-o*-phthalyl chloride should also act slowly, whereas experiments show that the opposite is the case. These differences in reactivity are explained by assigning a cyclic ketonic structure,

[50] R. Anschütz and W. Bertram, *Ber.*, 1904, **37**, 3967; *A.*, 1904, i, 972; compare Easterfield and Sell, *T.*, 1892, **61**, 1009.

[51] E. Ott, *Annalen*, 1912, **392**, 245; *A.*, i, 828.

$\begin{matrix}\cdot C\text{—}CO\\ \|\\ \cdot C\cdot CCl_2\end{matrix}\!\!>\!O$, to the malenoid dichlorides, the reaction between these substances and aniline being formulated thus:

$$\begin{matrix}R_1\cdot C\text{—}CO\\ \|\\ R_2\cdot C\cdot CCl_2\end{matrix}\!\!>\!O + NH_2Ph = \begin{matrix}R_1\cdot C\cdot C(OH)\cdot NHPh\\ \|\\ R_2\cdot C\text{————}CCl_2\end{matrix}\!\!>\!O \longrightarrow$$

$$\begin{matrix}R_1\cdot C\cdot CO\cdot NHPh\\ \|\\ R_2\cdot C\cdot COCl\end{matrix} + HCl$$

the remaining ·COCl-group reacting in the usual way.

Much evidence can be brought forward in support of this view as to the constitution of the malenoid dichlorides, for instance, the aluminium chloride compound of chlorofumaryl dichloride is a yellow mass, melting at 50°, and from which the chlorofumaryl dichloride is regenerated by treatment with water at 0°. If, however, the yellow mass is warmed, its colour deepens, and eventually becomes reddish-brown; the substance now melts at 100°, and is the aluminium chloride compound of chloromaleyl dichloride, because it yields this substance on treatment with water. This deepening in colour is in agreement with the formula now assigned to the malenoid dichlorides, since the aluminium chloride compounds of cyclic ketones are intensely coloured. The aluminium chloride compound of chloromaleyl dichloride, when heated at 180—230°, gives carbonyl chloride as one of its decomposition products, a result which strongly supports the cyclic formula, especially as no acid chloride has hitherto been known to give carbonyl chloride on heating. Further, the two carbonyl groups being in conjugated positions in the fumaroid dichlorides, should confer on these substances a degree of unsaturation much greater than that of the malenoid dichlorides, which have only one carbonyl group, and this conclusion is proved to be correct by experiment.

Chloromaleyl dichloride has been obtained in two forms, which can be easily converted into one another, and this observation supports the formula now assigned to this substance, since γ-lactones are frequently dimorphous. Lastly, the molecular volume of chlorofumaryl dichloride exceeds that of chloromaleyl dichloride by 4·4 units, which is in close agreement with the difference calculated on the assumption that the latter compound has a cyclic structure.

By the action of barium peroxide on an ethereal solution of acetic anhydride, Clover and Richmond[52] obtained acetic peroxide, and showed that this substance in aqueous solution gradually hydrolyses to molecular proportions of acetic acid and peracetic acid, and further, that the per-acid itself decomposes into acetic acid and hydrogen peroxide. These observers were, however,

[52] *Amer. Chem. J.*, 1903, **29**, 179; *A.*, 1903, i, 396.

unable to isolate the peracetic acid. It is now shown[53] that the reaction, $R{\cdot}CO{\cdot}OOH + H_2O \leftrightarrow R{\cdot}CO_2H + H_2O_2$, is reversible, and that the reaction in the direction right to left is brought into effect by the use of such catalysts as sulphuric acid, nitric acid, etc. In actual practice, the per-acid is best obtained by the interaction of the acid anhydride and hydrogen peroxide in the presence of sulphuric acid,

$$(R{\cdot}CO)_2O + H_2O_2 = R{\cdot}CO_2H{\cdot} + R{\cdot}CO{\cdot}OOH,$$

and subsequent distillation of the mixture under diminished pressure. The substance may also be conveniently prepared by decomposing the mixed anhydride of boric acid and the organic acid with hydrogen peroxide,

$$B(OAc)_3 + 3H_2O_2 = 3AcO_2H + B(OH)_3.$$

Peracetic acid is a clear, colourless, pungent liquid, soluble in water, alcohol, ether, or sulphuric acid. Its aqueous solution is comparatively stable, but acids, alkalis, and salts hasten its hydrolysis to hydrogen peroxide and acetic acid. It is extremely explosive, and when slowly heated to 110° it explodes violently. It attacks the skin, and acts as a powerful oxidising agent, converting aniline and *p*-toluidine into the corresponding nitroso-compounds, and manganese salts into permanganates. Perpropionic, perbutyric, and performic acids have also been prepared; the latter is not stable at the ordinary temperature, and could only be obtained as a 48 per cent. solution.

Hydrochloric or hydrobromic acid is capable of converting ferricyanic acid into ferrocyanic acid[54] with evolution of chlorine or bromine, which proves that the reaction:

$$2H_4Fe(CN)_6 + Cl_2 + Aq \leftrightarrow 2H_3Fe(CN)_6 + 2HCl + Aq,$$

is reversible. If the halogen is removed as quickly as it is formed, and this may be done by means of silver for the chlorine, and phenol or chloroform for the bromine, then the whole of the ferricyanic acid is converted into ferrocyanic acid. Theoretical considerations lead to the conclusion that the precipitate obtained by mixing solutions containing equivalent amounts of cupric and ferrocyanogen ions should have the same composition as that obtained under similar conditions from cuprous and ferricyanogen ions, and this is confirmed by experiment.[55] The precipitate obtained from cupric sulphate and potassium ferrocyanide has a constant composition only if one of the two components is in large excess; if the ratio $CuSO_4 : K_4Fe(CN)_6$ is greater than 2·5, then

[53] J. D'Ans and W. Frey, *Ber.*, 1912, **45**, 1845; *A.*, i, 601.

[54] C. Gillet, *Bull. Soc. chim. Belg.*, 1912, **26**, 236; *A.*, i, 614.

[55] E. Müller, G. Wegelin, and E. Kellerhoff, *J. pr. Chem.*, 1912, [ii], **86**, 82 *A.*, i, 614.

the precipitate has the composition $Cu''_2Fe''(CN)_6$, but if the ratio has a lower value, then the precipitate contains potassium as one of its constituents.

The electrolytic reduction of alkyl derivatives of ethyl acetoacetate has been regarded hitherto as taking place in accordance with the scheme:

$$CH_3\cdot CO\cdot CHR\cdot CO_2Et \longrightarrow CH_3\cdot CH_2\cdot CHR\cdot CH_3.$$

A careful comparison of the boiling points of the hydrocarbons resulting from these reductions with the boiling points of hydrocarbons of known constitution has led Tafel [56] to the conclusion that the reaction is not as expressed above, but that the methyl group resulting from the reduction of the carbethoxy-group occurs as part of the main chain and not as a side-chain. Thus, taking ethyl *iso*butylacetoacetate, $CH_3\cdot CO\cdot CH(CO_2Et)\cdot CH_2\cdot CHMe_2$, as an example, it should give, according to the old scheme, the hydrocarbon $CH_3\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CHMe_2$, the boiling point of which is 110°/763 mm. The boiling point of the product isolated was 117·5—118°/760 mm., which agrees with that of the hydrocarbons which would be formed according to the scheme now proposed by Tafel:

$$*CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{<}^{CH_3}_{CH_3} \leftarrow CH_3\cdot CO\cdot \underset{*CO_2Et}{CH}\cdot CH_2\cdot CH{<}^{CH_3}_{CH_3}$$

B. p. 116°/761 mm.

$$\longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot \underset{CH_3}{CH}\cdot CH_2\cdot {}^{*}CH_3$$

B. p. 117·6°/760 mm.

Wislicenus [57] is of opinion that of the four known forms of ethyl formylphenylacetate only two are chemically individual; these are: the liquid α-form, which is the enolic modification, $OH\cdot CH{:}CPh\cdot CO_2Et$, and the solid γ-form, m. p. about 100°, which is the enol-aldo-form, $CHO\cdot CPh{:}C(OH)\cdot OEt$. The other two forms: the β-modification (m. p. about 70°) and Michael's modification (m. p. about 50°), he regards as mixtures of the α- and γ-modifications. The modification melting at about 70° has been regarded hitherto as the true aldo-form, $CHO\cdot CHPh\cdot CO_2Et$, but Wislicenus's view as to its composition is supported by Meyer,[58] who finds that the compound is entirely enolic. Michael [59] is also of opinion that the solid modification melting at about 70° is a mixture, but recognises the existence of three forms of ethyl formylphenylacetate: the α-ester, boiling at 125—126°/9 mm.,

[56] *Ber.*, 1912, **45**, 437; *A.*, i, 234.
[57] *Annalen*, 1912, **389**, 265; *A.*, i, 623.
[58] *Ber.*, 1912, **45**, 2843; *A.*, i, 940.
[59] *Annalen*, 1912, **391**, 235, 275; *A.*, i, 861.

β-ester, melting at about 40°, and the γ-ester, melting at about 100°.

Michael's[60] statement that ethyl 1-methyl*cyclo*butan-3-one-1 : 2 : 4-tricarboxylate (I) is formed by the condensation of ethyl citraconate with ethyl sodiomalonate in alcoholic solution is now[61] shown to be incorrect, the substance actually formed being ethyl *cyclo*pentan-2-one-1 : 3 : 4-tricarboxylate (II):

$$\begin{array}{l} CO_2Et\cdot CH\text{---}CO \\ CO_2Et\cdot CMe\cdot CH\cdot CO_2Et \end{array}$$
(I.)

$$CO_2Et\cdot CH\!<\!\begin{array}{l} CH_2\cdot CH\cdot CO_2Et \\ CO\text{---}CH\cdot CO_2Et \end{array}$$
(II.)

If the condensation is carried out in such a manner that no considerable elevation of temperature occurs, then the product is ethyl butane-αββδ-tetracarboxylate,

$$CO_2Et\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CH(CO_2Et)_2.$$

This compound is, no doubt, an intermediate substance in the formation of the above *cyclo*pentanone, and its production by the condensation of ethyl citraconate and ethyl sodiomalonate is in all probability due to the action of traces of sodium ethoxide on the ethyl citraconate, whereby it is transformed into ethyl ethoxymethylsuccinate. This compound by the loss of alcohol gives ethyl itaconate, $CH_2{:}C(CO_2Et)\cdot CH_2\cdot CO_2Et$, which on condensation with ethyl sodiomalonate, in the normal way, gives ethyl butane-αββδ-tetracarboxylate.

The condensation of ethyl citraconate with ethyl sodiomalonate in ethereal solution has always been assumed to take place in accordance with Michael's positive-negative rule. According to Michael, the negative portion, $\cdot CH(CO_2Et)_2$, of ethyl sodiomalonate should attach itself to that carbon atom in ethyl citraconate to which the methyl group is joined, since this carbon atom, owing to the presence of the methyl group, is more positive than the other which has the hydrogen attached to it. The product would thus be ethyl β-methylpropane-ααβγ-tetracarboxylate:

$$CO_2Et\cdot CMe{:}CH\cdot CO_2Et \longrightarrow CH(CO_2Et)_2\cdot CMe(CO_2Et)\cdot CH_2\cdot O_2Et$$

This is now shown to be incorrect, and the compound actually formed when the condensation takes place in solvents like ether and benzene, which do not react with sodium, is ethyl butane-ααβγ-tetracarboxylate, $(CO_2Et)_2CH\cdot CH(CO_2Et)\cdot CHMe\cdot CO_2Et$. Rules like the one enunciated by Michael are of little value in determining the course of a condensation like the one under discussion. It seems much more probable that steric influence is the predominating factor in condensation of this type, there being generally great resistance to the formation of a quaternary carbon atom,

[60] *Ber.*, 1900, **33**, 3731; *A.*, 1901, i, 123; Michael and Schulthess, *J. pr. Chem.*, 1892, [ii], **45**, 55; *A.*, 1892, i, 591.

[61] E. Hope, *T.*, 1912, **101**, 892.

more especially if the groups involved have a large molecular magnitude.

Carbohydrates.

A new anhydride, anhydromethylglucoside, $C_7H_{12}O_5$, has been obtained by Fischer and Zach [62] by warming triacetylmethylglucoside bromohydrin with barium hydroxide solution. This anhydride distils undecomposed at very low pressure, forms a crystalline hydrate, and is not converted into sugar by emulsin, but acids hydrolyse it easily to a crystalline compound, $C_6H_{10}O_5$, which is regarded as an intramolecular anhydride of dextrose, and probably represents a new type of sugar derivative. It differs from the hexoses in that it restores the colour to Schiff's reagent, but strongly resembles them in many other respects, as, for instance, in its reactions with phenylhydrazine and alkalis, and in its behaviour on reduction and oxidation. The fact that the anhydrosorbitol obtained from it is isomeric with styracitol, a naturally occurring substance isolated by Asahina [63] from *Styrax obassia*, is evidence in support of the view that the anhydrides of dextrose and of glucosides occur in nature. Anhydrogluconic acid probably has an OH group attached to its γ-carbon atom, since it very readily forms a lactone; further, since the anhydrodextrose from which it is derived forms an osazone, it follows that the only formulæ possible for anhydrogluconic acid are limited to the three following:

$$CH_2\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO_2H,$$
$$\quad\ |\!-\!O\!-\!|$$

$$CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CO_2H,$$
$$|\!-\!\!-\!\!-\!

glucosamine may be derived from mannose, and not from glucose. Attempts to eliminate the amino-group from glucosamine by nitrous acid or the silver nitrite method of Fischer do not lead to a simple hexose, but to a hydrated furan derivative known as chitose. Now chitose also results from the dehydration of a hexose, and it was thought that if the hydroxyl groups in glucosamine were substituted the resulting compound would have its amino-group removed by the action of nitrous acid in the normal way, and that a derivative of the parent hexose would result. In the course of an investigation based on the above considerations, Irvine and Hynd [65] obtained a methylglucosamine, which at first appeared as if it might be identical with an aminomethylglucoside obtained by Fischer and Zach [66] from dibromotriacetylglucose. If these two compounds had proved to be identical, this would have meant the direct synthesis of glucosamine from glucose. A close comparison of the properties of these two compounds has shown, however, that they are not identical, but isomeric, and it is concluded that the methylglucosamine prepared by Irvine and Hynd is α-aminomethylglucoside, whereas in Fischer's aminomethylglucoside the amino-group may occupy the β-, δ-, or ε-position. As the conversion of α-aminomethylglucoside (methylglucosamine) into methylglucoside cannot be carried out directly, it was methylated by the silver oxide reaction, and thus converted into α-dimethylaminomethylglucoside, from which the dimethylamino-group was removed by heating with barium hydroxide. As the resulting methylglucoside could not be crystallised, it was completely methylated, and the tetramethyl methylglucoside purified by fractional distillation. The hydrolysis of this tetramethyl methylglucoside was effected in two stages: the first stage gave tetramethylglucose, the identity of which was proved by its melting point and specific rotation; and the second stage gave *d*-glucose, which was also fully identified by its specific rotation, and the specific rotation and melting point of its osazone.

The conversion of glucosamine into glucose by Irvine and Hynd [67] has thus been effected through the following reactions:

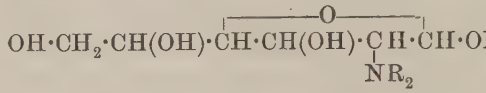
d-Glucosamine hydrochloride (from chitin obtained from lobster shells) → bromotriacetylglucosamine hydrobromide → triacetylaminomethylglucoside hydrobromide → aminomethylglucoside hydrochloride → methylaminomethylglucoside → dimethylaminomethylglucoside → [methylglucoside] → tetramethyl methylglucoside → tetramethyl glucose → *d*-glucose.

The evidence is in favour of the view that no Walden inversion

[65] *T.*, 1911, **99**, 250. [66] *Ber.*, 1911, **44**, 132; *A.*, 1911, i, 177.
[67] *T.*, 1912, **101**, 1128.

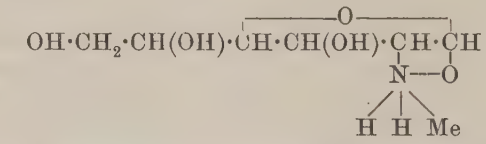
takes place during the series of changes which leads from *d*-glucosamine to *d*-glucose, and that the former must consequently be regarded as α-amino-*d*-glucose.

Constitution of α-Aminomethylglucoside and its Homologues.—The adoption of the formula



(where R = Me or H) for α-aminomethylglucoside and its *N*-alkyl homologues is, generally speaking, in accord with the properties of these substances. Several objections, however, can be raised against this formula; for instance, the very great difficulty with which it is hydrolysed, whereas such substances as α- and β-methylglucosides, Fischer's isomeric aminomethylglucoside, etc., are comparatively easily hydrolysed. This resistance to hydrolysis is intimately connected with both the presence and position of the nitrogen atom as shown by the remarkable fact that when treated with cold dilute nitrous acid it yields a product which has a vigorous action on Fehling's solution. The glucosidic part of the molecule thus seems to be affected whenever the amino-group is attacked.

This points to the existence of a betaine-like structure in the molecule, thus:



Evidence in support of this formula is afforded by the fact that both ammonia and methylamine are produced when the substance is heated with sodium hydroxide.

Only monohydric phenols have hitherto been used in the preparation of phenolic glucosides, although it is true that polyhydric phenols have been combined with sugars, but the products were of a complicated nature, and were not ordinary glucosides. Fischer and Strauss[68] have now succeeded in preparing phloroglucinol-*d*-glucoside by shaking an alkaline solution of phloroglucinol with an ethereal solution of acetobromoglucose, and subsequent removal of the acetyl groups. This synthetic glucoside is identical with the phloroglucinol-glucoside obtained by Cremer and Seuffert[69] by the action of barium hydroxide on phloridzin, and both are hydrolysed by emulsin. Phloroglucinol-glucoside is of physiological interest, because it is capable of producing diabetes. Resorcinol-

[68] *Ber.*, 1912, **45**, 2467; *A.*, i, 884. [69] *Ibid.*, 2565; *A.*, i, 885.

d-glucoside and 2:4:6-tribromophenyl-*d*-glucoside have also been prepared by a similar method.

The presence of maltose amongst the products of acid hydrolysis of starch has been denied by early workers, but in recent years Weber and Macpherson [70] and others have demonstrated the presence of as much as 20 per cent. and more of maltose in commercial glucose prepared by the acid hydrolysis of starch. This is now confirmed by Fernbach and Schoen,[71] who have isolated and completely identified maltosazone from the interaction of phenylhydrazine and the products of hydrolysis of starch mucilage by acids under pressure. These observers regard the processes of hydrolysis of starch by malt diastase and by acids as essentially identical, the only difference being that in the former case the hydrolysis stops at the maltose stage, whereas in the latter it goes a stage further.

When the sugars dihydroxyacetone, erythrulose, lævulose, sorbose, and perseulose in aqueous solution are exposed in quartz tubes to sunlight or ultra-violet light, they are decomposed into carbon monoxide, a little carbon dioxide, and the alcohol corresponding with the original sugar, but containing one carbon atom less. When starch in solution is exposed to *X*-rays it is converted into soluble starch and dextrin.[72]

The dehydration [73] of starch in a vacuum containing phosphoric oxide shows that at 25° as much as 28 per cent. of the starch is converted into water-soluble matter; this rises to 57 per cent. at 50°, and to 90 per cent. at 120°. The conversion of starch into dextrins is regarded as essentially a process of dehydration rather than hydrolysis, a supposition which is supported by the fact that a much better yield of dextrins is obtained when the starch is heated alone than when it is heated with water. Starch is regarded as consisting of molecular aggregates or complexes of $C_6H_{10}O_5$, which are held together by water, thus:

$$\{[(C_6H_{10}O_5\cdot OH)H]_n[(C_6H_{10}O_5\cdot OH)]_nH_{n-1}\}H\cdots.$$

In the process of dehydration the loss of water causes a breaking down of these complex aggregates into simpler ones, and it is thus that the various dextrins result.

Starch paste is converted by *Bacillus macerans* into substances

[70] *J. Amer. Chem Soc.*, 1895, **17**, 312; *A.*, 1895, ii, 296.

[71] *Bull. Soc. chim.*, 1912, [iv], **11**, 303; *A.*, i, 336.

[72] D. Berthelot and H. Gaudechon, *Compt. rend.*, 1912, **155**, 401; *A.*, i, 750; H. A. Colwell and S. Russ., *Proc. Physical Soc.*, 1912, **24**, 217; *A.*, i, 608; J. Bielecki and R. Wurmser, *Compt. rend.*, 1912, **154**, 1429; *A.*, i, 538; L. Massol, *ibid.*, 1645; *A.*, i, 538; J. Stoklasa, J. Šebor and W. Zdobnický, *Biochem. Zeitsch.*, 1912, **41**, 333; *A.*, i, 606; W. Löb, *ibid.*, 1912, **43**, 434; *A.*, i, 750.

[73] G. Malfitano and Mlle. A. Moschkoff, *Compt. rend.*, 1912, **154**, 443; *A.*, i, 240.

completely soluble in water, and from these two crystalline dextrins, α- and β-, have been isolated.[74] The α-isomeride crystallises in colourless, hexagonal plates or lancet-shaped needles, has $[\alpha]_D$ + 128°, and is doubly refractive; determination of its molecular weight by the cryoscopic method gave values corresponding with $(C_6H_{10}O_5)_4$. The β-isomeride crystallises in rhombic crystals, and has $[\alpha]_D$ + 136°; owing to its insolubility its molecular weight could not be determined. The generic term amylose is proposed for the polysaccharides having the formula $(C_6H_{10}O_5)_n$. On acetylation the α-isomeride gives a hexa-acetate, and the β-compound gives a nona-acetate, a result which shows that hydrolysis of the dextrins has taken place simultaneously with the acetylation. These acetyl derivatives on hydrolysis give respectively diamylose,

$$(C_6H_{10}O_5)_2,2H_2O,$$

and triamylose, $(C_6H_{10}O_5)_3,4H_2O$, each of which crystallises in needles and does not reduce Fehling's solution. The original α-dextrin is therefore tetra-amylose, and the β-dextrin, from its analogous behaviour to the α-compound, is regarded as hexa-amylose, $(C_6H_{10}O_5)_6$.

Gerber[75] has shown that hydrogen peroxide, even in very dilute solutions, is a very powerful agent for the hydrolysis of starch, the products being maltose and dextrins. If concentrated solutions of the peroxide are used, the maltose is oxidised.

Scyllite from the kidneys, etc., of certain plagiostomous fishes, quercine from acorns, and cocosite from *Cocos plumosa* and *Cocos nucifera*, are now shown to be identical, and it is proposed that in future they should all come under the heading "scyllitol."[76] The isomeric substance inositol has been obtained in two new forms: *iso*inositol and ψ-inositol.

Harden and Young[77] have published a detailed account of a method by means of which glycogen free from nitrogen, yeast-gum, and practically free (0·02 per cent.) from ash can be obtained from yeast. Details are also given for the isolation of the yeast-gum from the glycogen mother liquors.

When dry cotton[78] is submitted to the action of ozone (2 per cent.) a small quantity of carbon dioxide is evolved, and a cellulose peroxide and an acid derivative are formed; the properties acquired by the cotton as a result of this treatment being very similar to those possessed by cotton and linen which have been bleached by

[74] F. Schardinger, *Centr. Bakt. Par.*, 1911, ii, **29**, 188; *A.*, 1911, i, 181; H. Pringsheim and A. Langhans, *Ber.*, 1912, **45**, 2533; *A.*, i, 832.

[75] *Compt. rend.*, 1912, **154**, 1543; *A.*, i, 538.

[76] H. Müller, *T.*, 1912, **101**, 2383.

[77] ., 12, **101**, 1928.

[78] Miss M. Cunningham and C. Dorée, *ibid.*, 497.

chloride of lime and washed without the use of an "antichlor."[79] When the ozonised cotton is boiled with water or digested with alkali the acid derivative is removed, and the residual neutral product closely resembles the typical oxycelluloses. In the industrial method of bleaching by alternate treatment with ozone and bleaching powder, both the peroxide and the acid derivative play a part, the peroxide being decomposed by the bleaching powder, and the acid derivative increasing the activity of the bleaching powder.

When benzene is added to a solution of cellulose in sulphuric acid the hydrocarbon and the carbohydrate combine to form a compound which appears to have the composition $C_6H_7O_2Ph_3$; toluene, xylene, and ψ-cumene also form analogous compounds, for which the generic term desoxyn is proposed. The carbohydrate residue appears to enter the benzene nucleus in the para-position relative to the methyl group. Dextrose, like cellulose, also combines with benzene to produce a desoxyn, for which two formulæ are suggested: (1) $C_6H_7O_2Ph_3$, representing the anhydride of dextrose, in which three hydroxyl groups are replaced by phenyl groups; (2) $C_6H_6O_2Ph_2$, according to which the formation of the desoxyn would be represented by the equation:

$$C_6H_{10}O_5 + 2C_6H_6 - 3H_2O = C_{18}H_{16}O_2.$$

When a desoxyn is oxidised by permanganate it gives the aromatic acid corresponding with its aromatic constituent, thus: phenyldesoxyn gives 45 per cent. of benzoic acid, and tolyldesoxyn gives 20 per cent. of terephthalic acid.[80]

Mixtures of alcohols and ethers possess the property of dissolving certain varieties of nitrocellulose, although the latter compounds are insoluble in either component. Baker[81] has determined the viscosity of such mixtures, and concludes from his results that they contain an ether–alcohol complex, and to this complex he attributes the solvent power of the mixtures for nitrocellulose. Although the results show that dissociation of the alcohol,

$$(R{\cdot}OH)^n \rightleftarrows nR{\cdot}OH,$$

does take place, yet the function of the ether cannot be merely that of a dissociating solvent. For if this were so, and assuming that the solvent action is due to the non-associated alcohol, then it should be possible to replace the ether by other indifferent liquids without decreasing the solvent power of the mixtures, a deduction which experience proves to be incorrect. Further, if the solvent

[79] Cross and Bevan, *Zeitsch. angew. Chem.*, 1906, **19**, 2101.

[80] A. M. Nastukoff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 231, 505; *A.*, 1902, i, 362, 747; *Zeitsch. Farb. Ind.*, 1907, **6**, 70; *A.*, 1907, i, 413; A. M. Nastukoff and I. I. Kotukoff, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1152; *A.*, i, 762.

[81] *T.*, 1912, **101**, 1409.

action is dependent entirely on the dissociation of the alcohol, then the higher alcohols should prove better solvents than the lower ones, since they are less associated, whereas the opposite is the case.

Nitrogen Compounds.

Amines.—The new method for the separation of tertiary from secondary and primary amines which has been worked out by Hibbert and Wise [82] is based on the instability of the additive compounds of the Grignard reagent with tertiary amines, and is, briefly, as follows: To the mixture of amines, either alone or dissolved in ether, is added an excess of an ethereal solution of magnesium ethyl bromide (or methyl iodide), and the ether distilled off. The product is then heated in an oil-bath to 200—280° (depending on the nature of the amine), whereupon the pure tertiary amine distils over. The primary or secondary amine may be recovered from the residue by addition of sodium hydroxide and steam distillation.

The results of an investigation [83] of the action of acetyl chloride on various organic bases show that in the majority of instances an additive compound of the base and the acid chloride is the initial product; this is certainly always the case with tertiary bases, and the compound formed has the composition $R_3N,CH_3{\cdot}COCl$. This last statement is contrary to the view generally accepted that tertiary bases have no affinity for acid chlorides, and the compounds now described are the first of their kind.

Imino-compounds.—From the results of his researches on "the formation and reactions of imino-compounds," Thorpe [84] has formulated the following generalisations: (1) the imino-compounds react with sodium ethoxide in their amino-form only; (2) the β-imino-derivatives of the αγ-dicarboxylic esters are then derivatives of glutaconic ester, and conform, as such, to the third generalisation; (3) compounds containing the complex $X_2C{:}CR{\cdot}CH_2X$, in which X may be any negative group and R any univalent radicle or group, react with sodium ethoxide so as to retain the mobile hydrogen atom, and therefore yield sodium derivatives of the type

$$X_2C{:}CR{\cdot}\overset{*}{C}HNaX,$$

in which the mobile hydrogen atom is hepresented by (*). The replacement of the sodium in this compound by an alkyl group yields the alkyl derivative, $X_2C{:}CR{\cdot}CHRX$, and the action of sodium ethoxide on this substance causes the replacement of the mobile hydrogen atom, but the metal then takes up the most

[82] *T.*, 1912, **101**, 344.
[83] W. M. Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 1399; *A.*, i, 833.
[84] *T.*, 1912, **101**, 249.

negative position in the system, yielding the sodium derivative, $X_2CNa{\cdot}CR{:}CRX$. In certain cases the compound $X_2C{:}CR{\cdot}CNaRX$ is also formed, but to a small extent only. The following may be taken as an illustration: $CO_2Et{\cdot}CH(CN){\cdot}C(NH){\cdot}CH_2{\cdot}CO_2Et$ reacts as $CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CH_2{\cdot}CO_2Et$, which with sodium ethoxide and methyl iodide yields first $CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CHMe{\cdot}CO_2Et$, and then, by further action, a mixture of the two dimethyl derivatives, $CO_2Et{\cdot}CMe(CN){\cdot}C(NH_2){:}CMe{\cdot}CO_2Et$ and

$$CO_2Et{\cdot}C(CN){:}C(NH_2){\cdot}CMe_2{\cdot}CO_2Et.$$

Amides.—Storch,[85] by the oxidation of thiocarbamide, obtained a substance having the constitution

$$NH_2{\cdot}C(:NH){\cdot}S{\cdot}S{\cdot}C(:NH){\cdot}NH_2,$$

which is named formamidine disulphide by Fichter and Wenk,[86] who have recently obtained it by the electrolytic oxidation of thiocarbamide. The formation of this substance from thiocarbamide has been regarded as strong evidence in support of the unsymmetrical formula, $NH_2{\cdot}C(:NH){\cdot}SH$, for the latter. It is now shown by Werner[87] that the formation of the formamidine by oxidation of thiocarbamide by means of nitrous acid only takes place in the presence of a strong acid ioniser, such as nitric acid, sulphuric acid, etc.; and that if the oxidation be effected in the presence of acetic acid or other feeble acid ioniser, then the main product of the reaction is thiocyanic acid. To explain these and other facts Werner suggests a slight modification of the unsymmetrical formula for thiocarbamide, and proposes the formula $HN{:}C\!<\!\begin{matrix}NH_2\\|\\S\end{matrix}$, which represents the result of a combination between the acid group, ·SH, and the basic group, $\cdot NH_2$, of the unsymmetrical formula. This formula affords an explanation of the capability of thiocarbamide to form salts with the stronger acids only. Also weak acids would have no disturbing effect on such a compound, and the action of nitrous acid in the presence of a weak acid would be represented thus:

$$HN{:}C\!<\!\begin{matrix}NH_2\\|\\S\end{matrix} + HONO = HSCN + N_2 + 2H_2O.$$

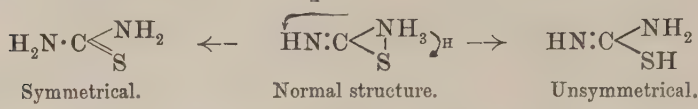
On the other hand, a strong acid, HX, would first form the salt

$$HN{:}C\!<\!\begin{matrix}NH_2,HX\\SH\end{matrix},$$

which would then react with nitrous acid to give formamidine disulphide and nitric oxide. The formation of nitrogen in the first case and of nitric oxide in the second are in complete agreement with experiment.

[85] *Monatsh.*, 1890, **11**, 452; *A.*, 1891, 548.
[86] *Ber.*, 1912, **45**, 1373; *A.*, i, 423.
[87] *T.*, 1912, **101**, 1167, 1982, 2166, 2180.

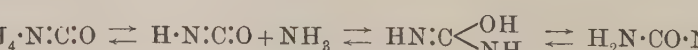
If the formula now proposed be accepted as representing the constitution of thiocarbamide under normal conditions, that is, in a neutral solution or even in the presence of a weak acid, then an explanation is afforded for the fact that thiocarbamide can give rise to products derived either from the symmetrical or unsymmetrical structure, thus:



Symmetrical. Normal structure. Unsymmetrical.

Dixon and Taylor[88] are of opinion that "thiocarbamide," together with its monohydric substitution derivatives containing hydrocarbon radicles not attached to sulphur, has the configuration represented by the typical formula $H_2N{\cdot}CS{\cdot}NH_2$; so long, at least, as these compounds remain in the static condition. They object to the formula $NH_2{\cdot}C(:NH){\cdot}SH$, because a substance having that constitution would be (1) probably very unstable, (2) a strongly marked base. The cyclic modification of this formula proposed by Werner is, in the opinion of the writer of this report, free from these objections.

The formation of carbamide from ammonium cyanate can no longer be regarded as entirely due to isomeric change; nor to an interaction between ammonium ions and cyanate ions, since ammonium cyanate in 90 per cent. alcohol is converted into carbamide about thirty times as fast as when dissolved in water; further, pure dry solid ammonium cyanate is readily transformed into urea when heated. The view that the carbamide results from the interaction between free ammonia and free cyanic acid has been put forward by Michael and Hibbert,[89] and is now supported by Chattaway,[90] who regards the interaction between these two substances as due to the tendency of the carbonyl group to add on groups such as $\begin{matrix}R\\R\end{matrix}\!>\!NH$ or $R{\cdot}OH$. Chattaway formulates the reaction thus:



The formation of alkyl-carbamides from *iso*cyanic esters, of carbamic esters from carbamide and alcohols, etc., can be explained in a similar way.

Wheeler[91] and others introduce the idea of partial valency to

[88] *T.*, 1912, **101**, 2502. [89] *Ann. Report*, 1909, 70.
[90] *T.*, 1912, **101**, 170.
[91] *J. Amer. Chem. Soc.*, 1912, **34**, 1269; *A.*, i, 752.

explain the interaction of ammonia and cyanic acid, which they express thus:

Amino-acids.—The glycerides of amino-acids when obtained will no doubt prove of great physiological interest, but all attempts to prepare these compounds have so far proved unsuccessful[92]; thus glycerol and glycine do not combine when heated alone or in the presence of hydrogen chloride or sulphuric acid, nor does silver glycine react with the monohalohydrins of glycerol. Bromo*iso*-valeric acid, sulphuric acid, and glycerol, however, interact when the mixture is heated at 70—80° to give bisbromo*iso*valerylglycerol, $OH{\cdot}CH(CH_2{\cdot}O{\cdot}CO{\cdot}C_4H_9Br)_2$, and it was thought that the bromine atoms in this compound would be readily replaced by the amino-group, but all attempts to do this by means of aqueous, alcoholic, or liquid ammonia only resulted in the hydrolysis of the compound and formation of a halogenated acid amide. When glycerol and an amino-acid are heated together, the glycerol appears to act as a dehydrating agent, with the result that the anhydride[93] of the amino-acid is formed; in fact, this is a convenient method for preparing these substances; thus an 80 per cent. yield of diketo-piperazine is obtained when glycine and four to five times its weight of glycerol are heated together at 170° for some hours. By the same method sarcosine and alanine are transformed into their cyclic anhydrides, and leucine into leucinimide.

A new and simple method for the separation[94] of betaine hydrochloride from molasses residue has been worked out by Stoltzenberg. It is based on the fact that whereas the solubility of the alkali chlorides and of glutamic acid hydrochloride is very much less in concentrated hydrochloric acid than in pure water, that of betaine hydrochloride is slightly greater in the former than in the latter solvent. The molasses residues are saturated with hydrogen chloride, and the precipitated alkali chlorides and glutamic acid hydrochloride, etc., filtered; the filtrate is concentrated, and alcohol added to the residue, when the betaine hydrochloride, which is sparingly soluble in alcohol, is precipitated. The method is applicable to the separation of betaine from other mixtures.

The aminotyrosine obtained by reduction of the nitro-compound resulting from the nitration of tyrosine is not 3-aminotyrosine,

[92] E. Abderhalden and M. Guggenheim, *Zeitsch. physiol. Chem.*, 1910, **65**, 53; *A.*, 1910, i, 226; R. Alpern and C. Weizmann, *T.*, 1911, **99**, 84.

[93] L. C. Maillard, *Compt. rend.*, 1911, **153**, 1078; *A.*, i, 13.

[94] *Ber.*, 1912, **45**, 2248; *A.*, i, 680.

but a mixture of this compound and its isomeride, 2-aminotyrosine.[95]

Amino-acids readily react with various sugars (dextrose, galactose, maltose, lactose, arabinose, etc.), with evolution of carbon dioxide and formation of cyclic condensation products, which appear to be identical with the melanin pigments obtained in the hydrolysis of proteins. If this identity is confirmed, it will provide an explanation for the comparatively low yield of amino-acids obtained in those cases where amino-acids and sugars are amongst the products of hydrolysis.[96]

A synthesis of racemic arginine from ornithuric acid (dibenzoylornithine) as a starting point has been effected by Sörensen, Höyrup, and Andersen.[97] If ornithuric acid is hydrolysed with warm concentrated hydrochloric acid δ-monobenzoylornithine is obtained, but by using $N/5$-barium hydroxide the δ-benzoyl group is removed, and the product is α-monobenzoylornithine,

$$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH\cdot COPh)\cdot CO_2H.$$

This on treatment with cyanamide and subsequent elimination of the benzoyl group gives

$$NH_2\cdot C(:NH)\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

which is found to be identical in every respect with racemic arginine. The isomeric δ-amino-*d*-guanidino-*n*-valeric acid was also prepared, and found to have quite different properties.

An important step in the determination of the constitution of the protamine clupeine[98] has been worked out. When this substance is nitrated a nitro-compound is obtained, which on hydrolysis yields nitroarginine; this nitroarginine on treatment with nitrous acid by van Slyke's process evolves nitrogen in amount corresponding with the decomposition of one amino-group. Since neither guanidine, nitroguanidine, nor clupeine itself gives nitrogen with this reagent, it follows that the amino-group in nitroarginine which is decomposed by the nitrous acid is not free in clupeine, but forms part of the main chain. Further, clupeine and guanidine behave similarly when nitrated, and have the same acid-fixing power. It follows, therefore, that the arginine groups in clupeine are linked up thus:

$$\cdots CO\cdot NH\cdot \underset{\displaystyle C_3H_6}{\underset{|}{CH}}\text{—}CO\text{—}NH\text{—}\underset{\displaystyle C_3H_6}{\underset{|}{CH}}\cdot CO\cdot NH\cdots$$
$$\qquad\qquad\quad NH\cdot C(NH)\cdot NH_2 \qquad NH\cdot C(NH)\cdot NH_2$$

[95] C. Funk, *T.*, 1912, **101**, 1004.
[96] L. C. Maillard, *Compt. rend.*, 1912, **154**, 66; *A.*, i, 169.
[97] *Zeitsch. physiol. Chem.*, 1911, **76**, 44; *A.*, i, 13.
[98] A. Kossel and A. T. Cameron, *ibid.*, 1912, **76**, 457; *A.*, i, 326.

Mercuric acetate (25 per cent. solution) in the presence of sodium carbonate is an efficient reagent for the precipitation of amino-acids.[99] The precipitate appears to be a basic salt of a carbamic acid formed from the amino-acid by the action of the sodium carbonate. The amino-acid is readily regenerated by the action of hydrogen sulphide on the mercury salt:

$$NH_2\cdot CH_2\cdot CO_2H \xrightarrow{Na_2CO_3} CO_2Na\cdot NH\cdot CH_2\cdot CO_2Na \xrightarrow{Hg(C_2H_3O_2)_2} \begin{matrix} NH{-}CO_2 \\ | \\ CH_2\cdot CO_2 \end{matrix}\!\!>Hg\cdot HgO \xrightarrow{H_2S} NH_2\cdot CH_2\cdot CO_2H + CO_2.$$

The methods available for the estimation of the amino-acids resulting from the hydrolysis of proteins give an approximate result only; in fact, in the majority of cases only about 60 per cent. of the protein is accounted for from the amount of amino-acids obtained. With the view of devising a more accurate method, Novák [1] has studied the action of methyl sulphate on several amino-acids, and finds that methylation occurs at both the nitrogen atom and at the carboxyl group, the action being similar to that of methyl iodide. With methyl sulphate, however, the action is almost quantitative, and much more easily carried out. An abnormal result was obtained with *l*-aspartic acid, which was converted almost quantitatively into fumaric acid.

That proline is a primary product of protein hydrolysis has now been definitely proved by its direct isolation as hydantoin from the products of fermentative hydrolysis of casein or gelatin.[1a]

Miscellaneous.

Carbon pernitride, $N{:}C\cdot N{<}\begin{matrix}N\\ ||\\ N\end{matrix}$ or $N{:}C\cdot N{:}N{:}N$, has been obtained [2] by the action of cyanogen bromide on a well-cooled aqueous solution of sodium azoimide; it forms colourless, odourless needles melting at 35·5—36°, and soluble in water and the ordinary organic solvents. It sublimes when heated in a vacuum just above its melting point, commences to decompose at 70°, and explodes very violently at 170—180°; since it is very sensitive to shock, it should be prepared in small quantities only. In aqueous solution it soon hydrolyses, giving azoimide and carbon dioxide as final products:

$$CN_4 \longrightarrow \begin{matrix}N\\ ||\\ N\end{matrix}\!\!>N\cdot CO\cdot NH_2 \longrightarrow \begin{matrix}N\\ ||\\ N\end{matrix}\!\!>N\cdot CO_2H \longrightarrow \begin{matrix}N\\ ||\\ N\end{matrix}\!\!>NH + CO_2.$$

[99] C. Neuberg and J. Kerb, *Biochem. Zeitsch.*, 1912, **40**, 498; *A.*, i, 540.

[1] *Ber.*, 1912, **45**, 834; *A.*, i, 337.

[1a] E. Abderhalden and K. Kautzsch, *Zeitsch. physiol. Chem.*, 1912, **78**, 96; *A.*, i, 492.

[2] G. Darzens, *Compt. rend.*, 1912, **154**, 1232; *A.*, i, 542.

When pure it is quite stable, but in the presence of traces of bromine it is converted into a polymeride insoluble in ether.

Pure diazomethane[3] has been obtained by the addition of an alcoholic solution of chloroform to a hot alcoholic solution of potassium hydroxide and hydrazine, a slow stream of nitrogen being passed through the apparatus, whereby the diazomethane is removed and then absorbed by ether:

$$H_2N{\cdot}NH_2 + CHCl_3 + 3KOH \longrightarrow >C{:}N{\cdot}NH_2 + 3KCl + 3H_2O$$
$$>C{:}N{\cdot}NH_2 \longrightarrow H_2C{:}N{:}N.$$

Pure diazomethane boils at $-24°$ to $-23°$, and is an extremely dangerous substance, exploding spontaneously or by contact with iodine, etc. When carbon monoxide is passed through a 1 per cent. ethereal solution of diazomethane and the gaseous mixture heated at 400—500°, the methylene resulting from the decomposition of the diazomethane combines with the carbon monoxide to form keten.

A solution of tetranitromethane in petroleum or other paraffin hydrocarbon gives intense colorations with compounds containing ethylenic linkings, and can be used as a delicate reagent for the detection of this class of substances.[4] The coloration is produced by unsaturated hydrocarbons, alcohols, ketones, ethers, esters, and aromatic substances, but not by aromatic nitro-compounds or by many unsaturated carboxylic acids. The enolic form of a tautomeric compound also produces a coloration with the reagent, whereas the ketonic form does not.

Ozonised oxygen produced by the silent electric discharge contains at least two allotropic modifications of oxygen, that is, ordinary ozone, O_3, and oxozone, O_4, the latter forming about one-third of the "crude" ozone.[5] When "crude" ozone is passed through sodium hydroxide and concentrated sulphuric acid, the oxozone is destroyed and the residual gas forms normal ozonides. The presence of oxozone in ozonised oxygen accounts for the formation of ozonides containing more oxygen than that corresponding with their degree of unsaturation, and also for the discordant results obtained by different workers when investigating the action of ozone on unsaturated compounds; thus Δ^{β}-butylene when treated with ozone, freed from oxozone by treatment with sodium hydroxide and sulphuric acid, gives the normal butylene ozonide, $O<\begin{matrix}O{\cdot}CHMe\\ |\\ O{\cdot}CHMe\end{matrix}$, and bisbutylene ozonide, $(C_4H_8O_3)_2$; the former is

[3] H. Staudinger and O. Kupfer, *Ber.*, 1912, **45**, 501; *A.*, i, 245.

[4] I. Ostromisslensky, *J. pr. Chem.*, 1911, [ii], **84**, 489; *A.*, i, 1.

[5] C Harries, *Ber.*, 1912, **45**, 936; *A.*, i, 407; *Annalen*, 1912, **390**, 235; *A.*, i, 673.

an oil with a stupefying odour, and the latter an odourless liquid, which explodes at 125°. With "crude" ozone Δ^{β}-butylene gives, not only the normal ozonide, but also butylene oxozonide, $C_4H_8O_4$, and bisbutylene oxozonide, $(C_4H_8O_4)_2$. By further treatment with "crude" ozone the normal butylene ozonide remains unchanged, whereas the bimolecular form is converted into bisbutylene oxozonide. When treated with boiling water all four substances are decomposed, and yield acetaldehyde, acetic acid, hydrogen peroxide, and oxygen.

As an example of the discordant results which have often been obtained in the past by different workers when studying the action of ozone on one and the same compound, we may take the case of the well-defined substance cholesterol. In 1908 Dorée and Gardner[6] obtained an ozonide from it, to which they gave the formula $C_{27}H_{46}O_4$; in the same year Diels[7] stated that the ozonide contained more oxygen, and that its formula was $C_{27}H_{46}O_5$; lastly, Molinari and Fenaroli[8] stated, also in 1908, that the ozonide which they had obtained had the composition $C_{27}H_{46}O_7$, and that consequently there were two double linkings in the cholesterol molecule.

Harries[8a] has recently investigated the action of ozone free from oxozone on cholesterol, and has shown that the ozonide has the composition $C_{27}H_{45}(OH)O_3$, thus confirming Tschugaeff's[9] statement that the cholesterol molecule contains only one double linking.

Bamberger and Suzuki[10] have obtained nitroglyoxime in the form of white, silky needles by the action of concentrated nitric acid on glyoxime dissolved in a mixture of ether and water. Since it appears necessary that the nitric acid should contain traces of nitrous acid it is probable that a nitroso-compound is first formed, which is subsequently oxidised by the nitric acid, the reduction of the latter affording a fresh supply of nitrous acid:

$$\begin{matrix} H\cdot C{:}N\cdot OH \\ | \\ H\cdot C{:}N\cdot OH \end{matrix} \xrightarrow{HNO_2} \begin{matrix} ON\ C{:}N\cdot OH \\ | \\ H\cdot C{:}N\cdot OH \end{matrix} \xrightarrow{HNO_3} \begin{matrix} O_2N\cdot C{:}N\cdot OH \\ | \\ H\cdot C{:}N\cdot OH \end{matrix}$$

That the substance is really a nitro-compound and not the nitrite (I) is very highly probable, since it does not give a typical Liebermann reaction, and can also be obtained by the action of nitrous acid on methazonic acid (II):

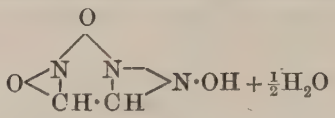
$$\begin{matrix} ON\cdot O\cdot C{:}N\cdot OH \\ | \\ H\cdot C{:}N\cdot OH \end{matrix} \qquad \begin{matrix} O_2N\cdot CH_2 \\ | \\ H\cdot C{:}N\cdot OH \end{matrix}$$

(I.) (II.)

Nitroglyoxime has certain properties characteristic of nitrolic acids, in that it dissolves in alkalis to a deep red solution, and gives

[6] *T.*, 1908, **93**, 1328.
[7] *Ber.*, 1908, **41**, 2596; *A.*, 1908, i, 728.
[8] *Ibid.*, 2785; *A.*, 1908, i, 882.
[8a] *Loc. cit.*
[9] *Annalen*, 1911, **385**, 352; *A.*, i, 30.
[10] *Ber.*, 1912, **45**, 2740; *A.*, i, 839.

deeply coloured salts. The substance $C_2H_3O_3N_3$, which Ulpiani obtained by the action of nitric acid on glyoxime, and which he regarded as a furoxan derivative of the constitution:



is now proved to be a mixture of nitroglyoxime and glyoxime.

The various methods available for the determination of the proportion of ketonic and enolic isomerides in a desmotropic compound were briefly described in last year's report.[11] One of these, the bromine β-naphthol process, has been applied recently by Meyer [12] to a large number of such compounds, with the following results: Keto-enolic tautomerism does not occur in crystalline substances, the crystals consisting of one form only. The modification in which a desmotropic substance exists in the crystalline state is not necessarily the one which will predominate in solution; thus dibenzoylacetylmethane is ketonic in the solid state, but in solution in alcohol or benzene over 90 per cent. of it is enolic; also methyl oxalacetate is enolic in the solid state, whereas the keto-form largely predominates in alcoholic solution. Acetaldehyde, acetone, pyruvic acid, and acetophenone, which contain one ·COR group, are present in alcoholic solution almost entirely in the keto-form, even in the presence of sodium ethoxide. A comparison of substances containing a methylene group attached to two ·COR groups (R = H, Me, Ph, OH, OMe, OEt, NH_2, CO_2Me, or CO_2Et) shows that in similarly constituted compounds the influence favouring enolisation exerted by various radicles increases in the order OMe, OEt, OH, NHPh, Me, Ph, CO_2Et, CO_2Me. Ethyl malonate consists entirely of the keto-form. Its sodium salt in methyl alcohol solution has the constitution $CO_2Et{\cdot}CH{:}C(ONa){\cdot}OEt$, and when it is acidified the resulting enolic modification of the ester very quickly changes to the ketonic form.

Tetramethylammonium amalgam [13] is obtained by the electrolysis of a solution of tetramethylammonium chloride in absolute alcohol kept at −34°, a mercury cathode being used. The resulting semi-solid product at the cathode is washed free from alcohol by carbon tetrachloride, and the liquid mercury removed by suction, when the amalgam is left as a silver-white, crystalline, metallic mass, which if kept at 0° under carbon tetrachloride undergoes very

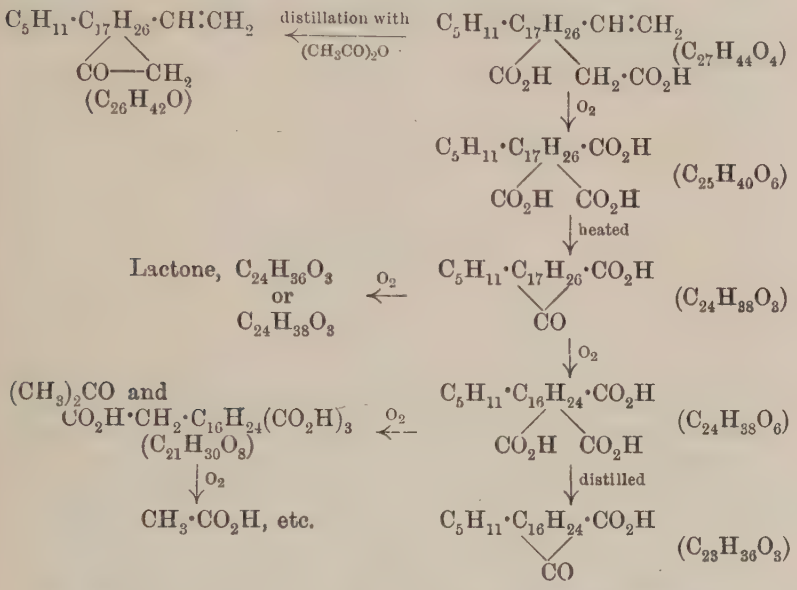
[11] *Ann. Report*, 1911, 100.

[12] *Ber.*, 1912, **45**, 2843, 2864; *A.*, i, 940, 941.

[13] H. N. McCoy and W. C. Moore, *J. Amer. Chem. Soc.*, 1911, **33**, 273; *A.*, 1911, i, 270; H. N. McCoy and F. L. West, *J. Physical Chem.*, 1912, **16**, 261; *A.*, i, 539.

little change in the course of several hours. During its spontaneous decomposition the amalgam emits negative electricity, and the residual mercury, if insulated, acquires a positive charge.

Cholesterol.—From the acid,[14] $C_{27}H_{44}O_4$, obtained by the oxidation of cholesterol, Windaus[15] has obtained the following degradation products:



The ketone $C_{26}H_{42}O$ is the next lower cyclic homologue of cholesterol, and since it is obtained by the distillation of the free acid, $C_{27}H_{44}O_4$, it follows that the two carboxyl groups in this acid are in a 1:6- or 1:7-position to each other; consequently, in cholesterol itself the ring containing the ·CH·OH-group must contain 6 or 7 carbon atoms. The conversion of the acid, $C_{25}H_{40}O_6$, into the ketonic acid, $C_{24}H_{38}O_3$, is analogous to the conversion of homocamphoronic acid into camphononic acid[16]; hence, in the acid $C_{25}H_{40}O_6$ the two carboxyl groups which disappear are also in the 1:6- or 1:7-position. Further, the formation of the tribasic acid, $C_{24}H_{38}O_6$, from the ketonic acid, $C_{24}H_{38}O_3$, shows that this substance has a ·CH_2-group next to the carbonyl group (compare conversion of camphononic acid into camphoronic acid[16a]), and so the mode of attachment of another carbon atom in the cholesterol molecule is ascertained. The formation of acetic acid by oxidation

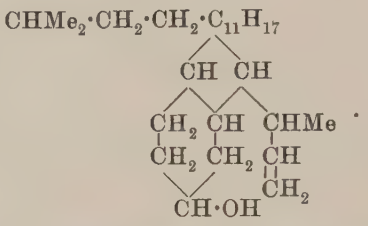
[14] Diels and E. Abderhalden, *Ber.*, 1904, **37**, 3092; *A.*, 1904, i, 880.
[15] *Ber.*, 1912, **45**, 1316, 2421; *A.*, i, 449, 854.
[16] Lapworth and Chapman, *T.*, 1899, **75**, 986, 1003. [16a] *Ibid.*

of the tetrabasic acid, $C_{21}H_{30}O_8$, shows that this acid contains a methyl group, and its formula may be written:

$$CO_2H\cdot CH_2\cdot C_{15}H_{21}\lessdot^{CH_3}_{(CO_2H)_3}.$$

A similar conclusion as to the presence of a methyl group in the $C_{17}H_{26}$ nucleus is arrived at by Minovici and Vlahutza,[17] who have obtained the acid $C_{26}H_{46}O_5$ by the action of hydrogen peroxide on chlolesterol.

The following formula for cholesterol is now proposed by Windaus:



The two resins, "jalapin," from the root of *Ipomoea orizabensis*, and "scammonin," from scammony root, have been hitherto regarded as identical substances, and as consisting of a homogeneous substance of glucosidic character. Both resins have now[18] been submitted to a very thorough chemical examination, and shown to be very complex substances, and to differ very considerably in their composition. They appear to consist to a large extent of the glucosides and methylpentosides of jalapinolic acid (hydroxyhexadecylic acid), $C_{15}H_{30}(OH)\cdot CO_2H$.

Hankow Chinese wood oil[19] on exposure to light in glass bottles fitted with air-tight stoppers gradually deposits crystals, which at the end of a year amount to about 6 per cent. of the oil. These crystals consist of the glyceride of β-elæostearic acid, and on hydrolysis yield the free β-elæostearic acid, $C_{18}H_{32}O_2$ or $C_{18}H_{30}O_2$, melting at 72°, of which several derivatives have been prepared. Both the free acid and its derivatives readily absorb oxygen on exposure to air, but although the ethyl ester soon gains 12 per cent. in weight, yet it does not set like the Chinese wood oil. The study of this crystalline glyceride may help to throw light on the changes which occur when a drying oil is exposed to air.

Fossek has shown that when the product of the interaction of phosphorus trichloride and an aldehyde, R·CHO, is treated with water, an acid of the type $R\cdot CH(OH)\cdot PO_3H_2$ is obtained. This

[17] *Bull. Soc. chim.*, 1912, [iv], **11**, 747; *A.*, i, 697.
[18] F. B. Power and H. Rogerson, *T.*, 1912, **101**, 1, 398.
[19] R. S. Morrell, *ibid.*, 2082.

work has been confirmed and extended by Page,[20] who has succeeded in preparing hydroxymethylphosphinic acid,

$$OH{\cdot}CH_2{\cdot}PO_3H_2,$$

by using paraformaldehyde or trioxymethylene instead of the formaldehyde itself.

Kipping[21] has revised the nomenclature of the organic derivatives of silicon, and suggested systematic names for the complex condensation products resulting from the silicanediols.

The same author[22] has succeeded in preparing pure diphenylsilicanediol, $SiPh_2(OH)_2$, by the hydrolysis of dichlorodiphenylsilicane. The isolation of the diol in a pure state presented exceptional difficulties, as the impurities were apparently adsorbed by the crystals. Pure diphenylsilicanediol usually decomposes and liquefies below 132°, but occasionally the decomposition does not occur below 160°. This apparently "double" melting point is not regarded as due to the existence of an isomeride, but is explained as follows: the crystalline form of diphenylsilicanediol, which separates from solvents at about 10—60°, decomposes and liquefies completely at about 128—132°, but near its melting point it is in a metastable state, and may, especially if certain impurities are present, change into another crystalline form, more stable at this higher temperature, which only decomposes at 160°; usually, however, the pure compound decomposes and liquefies before this change occurs. Perhaps the most characteristic property of diphenylsilicanediol is the ease with which it loses the elements of water, the presence of traces of alkalis or acids being sufficient to effect this loss, four well crystallised compounds having been isolated from the products of this change, namely:

(1) anhydrobisdiphenylsilicanediol, $HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$;

(2) dianhydrotrisdiphenylsilicanediol,

$$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH;$$

(3) trianhydrotrisdiphenylsilicanediol,

$$O\begin{<}{SiPh_2{\cdot}O}\\{SiPh_2{\cdot}O}\end{>}SiPh_2,$$

(4) tetra-anhydrotetrakisdiphenylsilicanediol,

$$O\begin{<}{SiPh_2{\cdot}O{\cdot}SiPh_2}\\{SiPh_2{\cdot}O{\cdot}SiPh_2}\end{>}O.$$

The study of the formation of analogous anhydrides from mixed diols like phenylbenzylsilicanediol, and also of mixed anhydrides from mixtures of, say, diphenylsilicanediol and dibenzylsilicanediol, will no doubt afford valuable information as to the structure of the complex inorganic silicates.

[20] *T.*, 1912, **101**, 423. [21] *Ibid.*, 2106. [22] *Ibid.*, 2108, 2125.

In a previous communication, Robison and Kipping[23] described the decomposition of dichlorodibenzylsilicane, $Si(CH_2{\cdot}C_6H_5)_2Cl_2$, and stated that the products were the isomerides α-dibenzylsilicol and β-dibenzylsilicol; the same authors[24] now show that the α-compound is dibenzylsilicanediol, $Si(CH_2{\cdot}C_6H_5)_2(OH)_2$, and the β-compound is an anhydro-derivative or oxide of dibenzylsilicanediol, crystallised with one molecule of water, and having the composition $HO{\cdot}Si(CH_2{\cdot}C_6H_5)_2{\cdot}O{\cdot}Si(CH_2{\cdot}C_6H_5)_2{\cdot}OH,H_2O$, and now named anhydrobisdibenzylsilicanediol.

H. R. Le Sueur.

Part II.—Homocyclic Division.

Although at the present time the difficulty of tracing the genesis of an idea in Chemistry in the vast literature is an excuse for the frequent claims to priority, which every journal contains, it seems indeed remarkable that fifty years ago a monograph,[1] in which not only was valency used in the modern manner, but also Kekulé forestalled by more than four years in the famous benzene formula, could entirely escape notice. Loschmidt's monograph, which has been rescued from forgetfulness by Anschütz,[2] will be deservedly placed among the "classics" of science. He recognises the "polarity" (localisation or direction) of valence, and states with rare lucidity the ideas which should be at the basis of the ordinary structural formulæ; the analogy between benzene and marsh gas as the first members of series, and the relation between the homologues and derivatives of the former were perceived at a time when no complete hand- or text-book of organic chemistry had been written, and the literature, especially of aromatic chemistry, was chaotic. That Kekulé was aware of Loschmidt's work is proved by his own words[3]; but it seems highly probable that he had only heard of the monograph from Kopp, who had come across it as editor of Liebig's *Jahresbericht*.[4] Although Loschmidt saw the possibilities of isomerism depending on the attachment of the substituent to a side-chain or the nucleus, he did not go so far as Kekulé in the recognition of the isomerism of the nuclear di- and tri-derivatives of benzene.

Structure of the Benzene Nucleus.—The fifty-two years which

[23] *T.*, 1908, **93**, 441. [24] *Ibid.*, 1912, **101**, 2142, 2156.

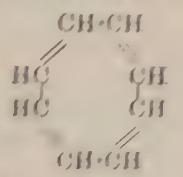
[1] J. Loschmidt, *Chemische Studien*, 54 pp., Wien, 1861.

[2] R. Anschütz, *Ber.*, 1912, **45**, 539; *A.*, i, 247.

[3] *Bull. Soc. chim.*, 1865, [ii], **3**, 100.

[4] 1861, 335.

have elapsed since Loschmidt recognised the molecule of benzene as formed of a remarkably stable ring of six carbon atoms, have added very little to our knowledge as to the exact structure of the benzene nucleus. Willstätter and Waser's[5] recent discovery of *cyclo*octatetraene has once more revived interest in the question:



This tetraene (like *cyclo*butadiene) is just such a closed system of an even number of alternating double and single linkings as is benzene. Yet in chemical properties it offers the most striking contrast, and behaves simply as a cyclic olefine; it reduces permanganate vigorously, and adds on bromine instantly; it takes up four molecules of hydrogen in the presence of platinum, and with nitric acid gives no substitution products, but becomes a tar. Moreover, on heating it is converted into stable, more saturated isomerides, probably by forming bridge linkings (see p. 145).

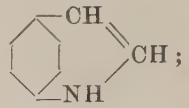
In the light of this great difference in character, Willstätter urges that there must be some fundamental difference in molecular structure. Thiele's theory of partial valence shows that the residual affinity of any closed system of alternating double and single linkings would be very much the same; and hence the chemical character of two such rings would not vary greatly with the number of atoms of which the ring is composed. Willstätter claims, therefore, that the discovery of *cyclo*octatetraene gives a final demonstration that Kekulé's formula is to be replaced by some other, and decides in favour of Armstrong's centric formula.[6] It is suggested that the tetraene cannot change into a similar centric configuration on account of the distance of the carbon atoms from the centre of figure.

The comparison of benzene, *cyclo*octatetraene, and naphthalene, more especially in their tendency to combine with hydrogen, leads Willstätter to the conclusion that Harries' formula for naphthalene (in which one ring only has a centric structure), based on its behaviour with ozone, is to be preferred.[7]

Another interesting observation on the character of compounds with a para-bridge-linking has been interpreted as indicating the centric structure of benzene. Although it is by no means unusual to find formulæ in which a bridge-linking is used, the undoubted

[5] *Ber.*, 1911, **44**, 3423; *A.*, i, 17. [6] *T.*, 1887, **51**, 264.
[7] *Annalen*, 1905, **343**, 311; *A.*, 1906, i, 225.

synthesis of one in spite of many attempts has only just been achieved by J. von Braun,[8] who has converted *p*-aminopropylbenzene into *p*-indole,



the complete similarity between the *p*- and *o*-indoles is held to be expressed only by a centric or diagonal structure of the nucleus.

The conceptions as to the exact relations of the carbon atoms in the benzene ring are naturally dependent on the precise views of valency on which they are based. Accepting the constant quadrivalency of carbon, and fixity of the directions in which the valency is exerted, the Kekulé formula represents benzene as having a much smaller ring tension, 2°35′, than a ring of six singly-linked carbon atoms, of which the ring tension is 5°16′, such as the hexamethylene ring, and the ring in the centric formula. The difference in reactivity between the Kekulé ring and the octatetraene ring may well be referred to this fact.[9] With the newer and less rigid conception of valency, the relation of the members of the ring may obviously be far more varied and elastic than is expressed by the usual alternative formulation. Moreover, a dynamic rather than a static structure has in addition been relied on to account for many of the properties (mainly optical) of the aromatic series; thus largely on the ground of the peculiar optical properties (fluorescence, etc.) of aromatic compounds, von Liebig [10, 11] urges that at the double linkings in benzene, a continuous rocking motion is to be found (a suggestion which differs little from many earlier ones), whereas in the tetraene, which is of yellow colour, there are two pairs of double linkings each analogous to the pair in a benzoquinone; the oscillations at the four double linkings do not fall into the rhythm characteristic of benzene, and hence the difference in chemical character.

In Thiele's and Armstrong's benzene formulæ, the original valency theory is extended, if not abandoned; in the former each carbon atom is quinquevalent, and in the latter each has a general attachment to the five other carbon atoms. On the basis of Werner's theory of a universal affinity acting in all directions from atomic centres, a new way of representing the peculiar properties of the benzene ring is described in an interesting paper by Böeseken.[12] In

[8] *Ber.*, 1912, **45**, 1274; *A.*, i, 497.

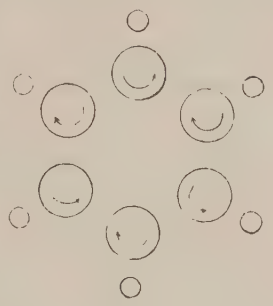
[9] J. Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 1066; *A.*, i, 430.

[10] *J. pr. Chem.*, 1912, [ii], **86**, 175; *A.*, i, 686.

[11] R. Casares, *Anal. Fis. Quim.*, 1912, **10**, 14; *A.*, i, 247.

[12] *Loc. cit.*

order to account for the union of two like atoms to form a molecule, a certain difference analogous to that between optical isomerides, which is not a difference in energy, must exist. This difference is represented by opposite rotations of the atoms, a devise by which a "dynamic" condition can also be simply expressed.[13] When applied to the benzene ring, this idea is symbolised as in the annexed figure. It will be seen that the contrast between the ortho- and para- on the one hand, and the meta-position on the other, is shown, and, moreover, the equality of the two ortho-positions. When a carbon atom is attached to the maximum four atoms or groups, they occupy the angles of a tetrahedron. If, however, three atoms or groups are attached to a carbon atom, since, following Werner, a fixed valency direction does not exist, the three atoms will, to obtain the simplest arrangement, lie in one plane grouped round the carbon. Hence it is conceived that the six carbon and six hydrogen atoms of benzene lie in one plane, when in a configuration of most stable equilibrium, and that the unsaturation or residual affinity is evenly distributed over the whole molecule. Less clearly defined, but somewhat similar, views are expressed by H. Kauffmann[14] in the statement of his auxochrome theory (see p. 137).



The best test of this formulation is its ability to bring into harmony the various facts of substitution, and the other reactions of benzene; thus a particular advantage of the centric formula, and to a certain degree of Thiele's modification of Kekulé's, is that they represent the great change of properties on adding a molecule of hydrogen to such a derivative as terephthalic acid. In the unsubstituted benzene the even distribution of affinity will tend to prevent the local addition of chlorine or bromine, which may precede substitution; and, in the absence of a catalyst, it has been found that even when the benzene is in excess the additive benzene hexahaloid is alone produced.[15] The addition of hydrogen to naphthalene and other condensed rings may be an example of local addition, but here there is a possibility of a less even distribution of residual affinity. Whether, however, substitution in benzene by halogens in the absence of a catalyst is preceded by local addition must at present be left an open question; the primary additive

[13] *Rec. trav. chim.*, 1910, **29**, 86.

[14] *Ber.*, 1906, **39**, 1959; *A.*, 1906, i, 841; "Die Valenzlehre," 1911.

[15] T. van der Linden, *Ber.*, 1912, **45**, 231; *A.*, i, 174.

products have not been isolated at least in this case.[16] The existence of a very large number of additive compounds of the usual catalysts with hydrocarbons, which have been recently studied,[17] suggests that the catalyst acts by modifying rather the benzene than the halogen. The disturbance of the even distribution of the affinity by the catalyst will render easy the local addition of halogen. The subsequent elimination of hydrogen bromide would obviously be accompanied by a considerable fall of chemical potential, but the catalyst may also accelerate this part of the process of substitution. In the case of nitration and sulphonation the evidence is clear that the agents themselves provide the catalyst, which is most probably the anhydride of the acid.

In a monosubstituted benzene the residual affinity can no longer be evenly distributed, a fact which may be expressed in Böeseken's diagram or by modifications of Kekulé's formula in the manner suggested by Flürscheim [18] by the help of partial or subsidiary valence. The presence of a group, X, attached to carbon at one end of the conjugated double linkings, 1,6 and 5,4, will affect the power of addition at positions 1 and 4 and at the positions 1 and 6, but not, or not to such an extent, at the positions 2 and 3 [19]:

X

The mere presence of the group for this reason favours ortho-para- rather than meta-substitution. Substitution will occur in the three positions, but with very different velocities, which will vary with the nature of X, and hence produce different proportions of the three di-derivatives in the final products. The results of the nitration of many monosubstituted benzenes give excellent illustrations of this proposition.

A second factor has to be taken into account, namely, the attraction exerted by X on the substituting agent. When this is sufficiently great the group X will be chemically changed, as in the

[16] A. F. Holleman and J. Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **18**, 535; A. Werner, "Neuere Anschauungen," 2nd. Ed.; E. Fischer, *Annalen*, 1911, **381**, 123; *A.*, 1911, i, 418; W. Manchot, *Annalen*, 1912, **387**, 257; *A.*, i, 230.

[17] Among others, B. N. Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1275, 1785, 1303, 1329, 1805; *A.*, i, 98, 99, 100, 177, 193; P. Pfeiffer, *Annalen*, 1911, **383**, 92; *A.*, i, 788.

[18] *T.*, 1909, **95**, 718; *ibid.*, 1910, **97**, 84.

[19] A. F. Holleman, "Die direkte Einfuhrung von Substituenten in den Benzolkern," 1910; Holleman and Böeseken, *loc. cit.*; J. Obermiller, "Die orientierenden Einflüsse und der Benzolkern," 1909.

reduction of the nitro-group, oxidation of the thiol group, etc., or will form only unstable additive products, which have occasionally been isolated, especially in the case of amines.[20] The attraction between X and the agent may, however, under the given conditions fall short of reaction or addition, and only result in a very rapid ortho-para-substitution, for example, when X is hydroxyl in phenols; or the attraction may be still slighter and meta-substitution accompany the ortho-para, as in toluene, the process now having a smaller velocity. Finally, the nature of X (for example, a nitro-group) may be such as to inhibit substitution, whence it follows the position, 2,3, which is least under its influence, will be attacked, and meta-substitution, which is always a relatively slow reaction, predominate. It is obvious that in the addition to the 2,3 linking, at least some ortho-derivative should be formed; and exact work has demonstrated that, at least so far, pure meta-substitution has not been observed.[21] Although the group X may inhibit the action of the ordinary substituting reagents, it may yet render the benzene derivative more accessible to others; then, however, an ortho-para-reaction will follow. As examples will serve the replacement of chlorine by hydroxyl when ortho-para to a nitro-group, and the ready reduction of benzoic acid and still more phthalic acid (to $\Delta^{3:5}$-dihydrophthalic acid) in the ortho-para-positions by hydrogen. (These are also examples of the primary local addition.) The reaction (or union) of the substituting agent with the group X, and the fact that the products can often be converted into nuclear derivatives (sometimes isomeric, as, for instance, nitroaminobenzenes and nitroanilines, benzoyl nitrate, and *m*-nitrobenzoic acid) has resulted in the popular opinion, which so often finds expression in the literature, that these substances are necessary intermediaries, and that the conversion, when it occurs, is intramolecular. An intramolecular change may occur in this as in other reactions, but the evidence that such is the case must be forthcoming.[22]

The foregoing gives a very brief summary of the views at present held by those who are now engaged in studying the problem of substitution in aromatic compounds. It cannot be said that the recent exposition of the mechanism of substitution in benzene contains much that was not embodied in earlier conceptions[23]; the

[20] H. Wieland, *Ber.*, 1907, **40**, 4260; *A.*, 1907, i, 1076; *ibid.*, 1910, **43**, 699; *A.*, 1910, i, 242.

[21] A. F. Holleman and collaborators, *loc. cit.*; and *Ber.*, 1911, **44**, 704; *Rev. trav. chim.*, 1911, **30**, 48; *Bull. Soc. chim.*, 1911, [iv], **9**, i; *Ber.*, 1911, **44**, 2504, 3556; *A.*, 1911, i, 364, 535, 713, 849; 1912, i, 20.

[22] *Brit. Assoc. Reports*, 1910, 85; *Science Progress*, 1909, **4**, 213.

[23] Armstrong, *ibid.*, 1899.

newer views on valency have given freedom, and exact quantitative work has brought precision, but the fundamental ideas are little modified.

Nitro-compounds.

The study of the absorption spectra[24] of a very large number of nitro-compounds, and of their metallic and alkyl derivatives, has brought to light some very striking facts with regard to the isomerism of this group. Up to the present there was no doubt that two desmotropic forms existed, the true nitro-group, $\cdot NO_2$, and the *iso-* or *aci*-nitro-group, present always in the salts, to which various constitutions have been assigned. The Michael-Nef formula, $RR'C{:}NO{\cdot}OH$, is more generally accepted, although the formula $RR'C{\cdot}N{\cdot}OH$ (with O), originally put forward by Hantzsch, finds some adherents[25]; but the reactions, which have been urged as evidence for the latter, are those exhibited by compounds in which other negative groups (carbonyl, phenyl, etc.) are present, and hence may be due rather to the general character of the compound than to the particular arrangement of the nitro-group.

The spectroscopic investigations of Hantzsch[26] have convinced him that a third type of nitro-compound exists, the "conjugated *aci*-nitro"-compound. In the spectra the three types are distinguished in that the true nitro-compound has a feeble selective absorption, the *aci*-nitro-compound feeble general absorption, and the "conjugated" *aci*-nitro-compounds very strong selective absorption. The simple *aci*-nitro-compounds are only found in the otherwise unsubstituted nitro-paraffins. The conjugated is the invariable form of the salts whenever a negative (unsaturated) group (NO_2, $CO\cdot$, CO_2H, Ar, CN, etc.) is combined with the carbon atom which bears the nitro-group; and it is found uncombined as well as in salts, esters, etc. So fundamentally different are the spectra of the "conjugated" *aci*-nitro-compounds from the other two classes, and at the same time so little affected by the character of the compounds in which they are present, that Hantzsch urges the existence of some peculiar and characteristic constitution. A six-membered ring, which is constructed with the aid of a sub-

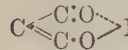
[24] Absorption spectra are now so universally described that reference cannot be made here to all the papers, but attention may be directed to a research dealing exclusively with the subject of this paragraph. G. T. Morgan and collaborators, *T.*, 1911, **99**, 1945; *ibid.*, 1912, **101**, 1209.

[25] W. Steinkopf and B. Jürgens, *J. pr. Chem.*, 1911, [ii], **84**, 686; *A.*, i, 152.

[26] A. Hantzsch and K. Voigt, *Ber.*, 1912, **45**, 85; *A.*, i, 151.

sidiary valence, is this chromophore, and is represented in typical examples, thus:

In no case has a simple *aci*-nitro-form been observed when the "conjugated" *aci*-nitro-ring is capable of existence; the equilibrium is directly between the true nitro- and the conjugated *aci*-nitro-forms, and not through the *aci*-nitro, thus:

This fact, and the far-reaching optical and chemical analogy between the negatively substituted ketones and the conjugated *aci*-nitro-compounds, has led Hantzsch to modify his former opinion as to the relation between the ketones and the salts of the enolides, which are classed as similar "conjugated" compounds,  , in that an intermediary true enolide is now regarded as superfluous. The equilibrium is dependent on the nature of the medium, the dilution, and the temperature, and hence Beer's law is not applicable to these solutions.[27] Ionisation is, as usual, not recognisable optically; both the ion and the non-ionised compound show the same absorption.

The chromoisomeric salts of nitro-compounds have the typical spectra of the conjugated *aci*-nitro-form. Hence the earlier opinion that it was the isomerism of *aci*-nitro- and conjugated *aci*-nitro-compounds is abandoned, and since polymorphism is excluded, the author falls back on valency-isomerism, thus:

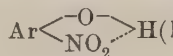
Moreover, grounds are advanced for the existence of an equilibrium between the two forms in solution. It is, however, highly significant that a compound which shows this chromoisomerism does not show the equilibrium with the isomeric true nitro-compound; and, conversely, where this type of isomerism is observed, chromoisomerism does not exist. It is here, perhaps, that the weak spot in this otherwise wonderfully clear-cut and convincing theory lies.

The nitrophenols offer a very good example of the manifold relations of the nitro-group; it is only, however, in the para-series that the behaviour can be interpreted.[28] *p*-Nitrophenol and the

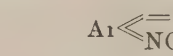
[27] J. Piccard, *Annalen*, 1911, **381**, 347; *A.*, 1911, ii, 561; A. Hantzsch, *Annalen*, 1911, **384**, 135; *A.*, 1911, ii, 951.

[28] See also W. P. Dreaper, *T.*, 1911, **99**, 2094.

stable series of ethers have typical conjugated *aci*-nitro-spectra, and hence have the structure (I) of these compounds. The salts and the red labile esters exert, however, a far stronger absorption, and hence they are given a quinonoid constitution, and at the same time a new position for the subsidiary valence (II):



(I.)



(II.)

A neat demonstration [29] that salt formation in aromatic nitro-compounds only causes the special type of absorption just referred to, when a quinonoid rearrangement is possible, has been given in a comparison of the spectra of the following substances in neutral or alkaline media: *p*-nitrobenzoic acid, phenylacetonitrile and phenylacetic acid, with those of *p*-nitrophenylacetonitrile, ethyl *p*-nitrophenylacetate, and finally *p*-nitrophenylacetic acid. In the first group the spectra of the two solutions are practically identical, but in the second group a characteristic additional band appears in the alkaline solution. In the case of *p*-nitrophenylacetic acid this change is only observed in the presence of considerable excess of alkali, as a salt of the type $NaNO_2{\cdot}C_6H_4{\cdot}CH{\cdot}CO_2Na$ would be extensively hydrolysed.

A constitutively unchangeable nitro-compound,[30] which yet exhibits intense colour, has been found in 4′-nitro-2:5-dimethoxybenzophenone. The authors find in it an excellent illustration of Kauffmann's theory (see p. 137) of the division of the valence-unit, brought about in this case by the interaction of the nitro- and methoxy-groups, as the cause of colour.

Another interesting observation,[31] which may be related to that last mentioned, is the final demonstration that there are two distinct *o*-dinitrobenzidines, yielding distinct acetyl derivatives and distinct dinitrodiphenyls. It is suggested that this is another case of the isomerism, referred to in other places in this report, which depends on the limitation of the free rotation of singly-linked carbon atoms.

Some researches which cannot be dealt with at length show that much is yet to be learnt about the reduction of nitrobenzene by various methods.[32, 33]

[29] J. T. Hewitt, F. G. Pope, and Miss W. I. Willett, *T.*, 1912, **101**, 1770.

[30] H. Kauffmann and A. de Pay, *Ber.*, 1912, **45**, 776; *A.*, i, 365.

[31] J. C. Cain, A. Coulthard, and Miss F. M. G. Micklethwait, *T.*, 1912, **101**, 2298.

[32] R. C. Snowdon, *J. Physical Chem.*, 1911, **15**, 797; *A.*, i, 100.

[33] E. F. Farnau, *ibid.*, 1912, **16**, 249; *A.*, i, 436; H. C. Allen, *ibid.*, 131; *A.*, i, 249.

Diphenylamine.

The chemistry of the well-known blue reaction of diphenylamine with nitric acid and other oxidising agents [34] has been up to the present mainly a matter of speculation; the most attractive hypothesis was that the salts of the halochromic diphenylhydroxylamine [35] produced the colour.

Although the first product of the oxidation of diphenylamine is tetraphenylhydrazine,[36] which in an acid medium yields diphenylbenzidine,[37] yet H. Wieland came to the conclusion [38] that the tetrahydrazine was hydrolysed to diphenylamine and diphenylhydroxylamine, which then condensed, and finally oxidised to the *o*-quinonoid sulphate of a phenazine:

$$C_6H_4<\begin{matrix}NPh(O\cdot SO_3H)\\NPh(O\cdot SO_3H)\end{matrix}>C_6H_4,$$

a compound the constitution of which now seems extremely doubtful. Kehrmann [39] has now demonstrated that the diphenylbenzidine is undoubtedly formed under the usual conditions of the reaction, and, moreover, yields with oxidising agents an intensely blue salt of a haloquinoneimonium type:

which was isolated as the platinichloride. The cause of the colour reaction is to be found in the formation of this compound.

Keto-enol Isomerism.

During the year the results of some extremely interesting and important researches on this subject have been published; the increasing power and delicacy of the agencies at the command of chemists is particularly well illustrated in the advances which have recently been made in this difficult subject.

The methods which can now be used, not only for the recognition of a compound as an enolide or ketone, but for the quantitative estimation of a mixture, are various. Of the chemical methods the ferric chloride colour reaction with the enolide (Wislicenus) is only applicable when the transformation takes place very slowly, for this reagent disturbs the equilibrium by its powerful catalytic acceleration of the enolisation. Claisen's method of

[34] Merz and Weith, *Ber.*, 1872, **5**, 283.
[35] A. von Baeyer, *ibid.*, 1905, **38**, 583.
[36] F. D. Chattaway and H. Ingle, *T.*, 1895, **67**, 1090.
[37] V. Kadiera, *Ber.*, 1905, **38**, 3575; *A.*, 1905, i, 934.
[38] *Annalen*, 1911, **381**, 200; *A.*, 1911, i, 569.
[39] F. Kehrmann and St. Micewicz, *Ber.*, 1912, **45**, 2641; *A.*, i, 1020.

extracting the enolide by a dilute solution of sodium carbonate is confined to solids, and is useless for solutions or liquid mixtures. The reaction with tertiary amines [40] may give correct results in isolated cases, but is certainly not generally applicable. The method of bromination [41] in its improved form [42] is not only exceedingly trustworthy, but can be used for liquid, solid, and solution with equal ease. A high speed of enolisation would, however, as in all chemical methods, invalidate the conclusions as to the composition of the equilibrium mixture, and for this reason it has not been found applicable in the case of the phenylindandiones.[43]

Of the physical methods, the molecular refraction (Brühl) has been shown recently by Auwers [44] to be susceptible of exact quantitative application: where comparisons are possible and close agreement has been found between this and the bromine method. The absorption spectrum appears, however, to be the most delicate method when the equilibrium in solutions is to be examined, and has recently been used with great success by Hantzsch (*loc. cit.*).

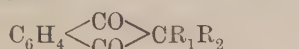
By means of the method of bromination, K. H. Meyer has made an exact study of a large number of substances, and of the equilibrium between the keto- and enol forms in the molten state or in solution. It is now possible to state approximately the relations between the constitution and the relative proportions of the two forms in an equilibrium mixture.

Such equilibrium mixtures are only found in the liquid or dissolved, but never, as has been suggested, in the crystalline state; the solid consists of one form only. If the solid (ketone or enolide) is the metastable, it will gradually change completely into the stable form; so far a transition point where coexistence would be possible has not been observed. Stability of one form in the solid state bears no relation to the composition of the equilibrium mixture, either in the molten state or in solution; thus the stable ketone, acetyldibenzoylmethane, $(C_6H_5{\cdot}CO)_2CH{\cdot}CO{\cdot}CH_3$, in alcohol is enolised to the extent of 90 per cent. The nature of the solvents has, of course, a great influence; for example, methyl benzoylacetate is enolised to the extent of 0·8 per cent. in water, 13·4 in methyl alcohol, 15·3 in chloroform, 69 in hexane, and 16·7 when molten. The value of the ratio (K/K') of the equilibrium constants (equilibrium constant $= K =$ [enolide]/[ketone]) of any two compounds, at least when similarly constituted, is nearly the same

[40] A. Michael and H. D. Smith, *Annalen*, 1908, **363**, 20; *A.*, 1908, i. 943.
[41] *Ann. Report*, 1911, 101.
[42] K. H. Meyer, *Ber.*, 1912, **45**, 2843; *A.*, i, 940.
[43] A. Hantzsch, *Annalen.*, 1912, **392**, 286; *A.*, i, 869.
[44] K. Auwers, *Ber.*, 1911, **44**, 3530; *A.*, ii, 3.

whatever the medium; thus the value of K for methyl benzoylacetate is about 2·2 times as great as the value of K for ethyl acetoacetate. Moreover, the same relation holds often, but not so uniformly, for the molten state.

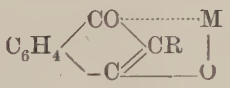
Indandiones and Oxindones.—The keto-enol isomerism of the indandiones and bisindandiones (II) has been fully investigated by Hantzsch and his pupils,[45] mainly with the aid of the absorption spectra:



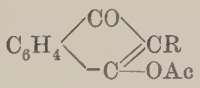
(I.)

(II.)

The absorption spectra of the indandiones of the type I, which are nearly colourless and not capable of enolisation, are continuous, and not markedly or sharply affected by the nature of the solvents or substituents. On the other hand, the indandiones containing the group ·CO·CHR·CO· yield salts exhibiting selective absorption which are oxindone derivatives, ·C(OH):CR·CO·. These indandiones, like ethyl acetoacetate, have in solution very variable spectra; in the active solvents (alcohol, etc.) enolisation is shown by the selective absorption, whilst in indifferent solvents the colour fades and the general absorption, typical of ketones, is observed. As will be seen, these relations are the converse of those found to hold with the ketonic esters, where enolisation is most prominent in indifferent media. A comparison of the spectra of the salts with other enolic derivatives has led Hantzsch [46] to suggest that the former have a peculiar structure, with the metal attached by a subsidiary valence to the carbonyl group as well as to the oxygen (III):

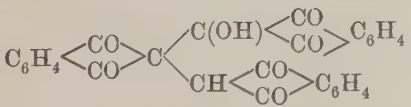


(III.)



(IV.)

This type is called the "conjugated" enolide. The new observations on indandiones, etc., afford strong confirmatory evidence for this suggestion. The acyl-oxindones, which are also enolic derivatives of the indandiones (IV), show spectra in which the selective absorption is both less and simpler than in the salts. In the bisindandiones and the hydroxytrisindandiones:



the enolides and the enolic ethers have spectra resembling, and

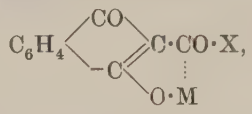
[45] *Annalen*, 1912, **392**, 286, 302, 319, 322, 328; *A.*, i, 869.

[46] *Ann. Report*, 1910, p. 80.

often identical with, the salts, a fact which is interpreted as evidence for a "conjugated" structure in these compounds as well as in the salts. The formula (III) shows that in the conjugated structure a six-membered ring exists; to this is attributed the peculiar absorptive power as a consequence of a "strong isorropesic state of vibration" ("lebhafte isorrhopische Schwingungszustand"). The two types of salts, both enolides, which certain indandiones yield, are distinguished by the form of this "conjugated" ring. The indandiones, in which R in the group

$$\cdot CO \cdot CHR \cdot CO \cdot$$

is an alkyl radicle, produce red salts having high selective absorption, whilst those in which R is an acyl radicle or contains a carbonyl group, yield yellow salts, the selective absorption of which is feebler. This difference is attributed to the absence of the six-membered ring in the yellow salts, which have instead as a chromophoric group a five-membered ring, thus:



also possessing a subsidiary valence.

The peculiar existence of isomeric ketonic modifications of 1:3-diketones has been studied by Michael[47] and his collaborators in the case of dibenzoylacetylmethane and dibenzoylpropionylmethane. In both cases the more stable ketonic form (β) is converted into a second (γ) by treatment with acetyl chloride. These two compounds are both unimolecular, and have widely different melting points. Since this isomerism cannot be accounted for by the usual formulæ, it is suggested that it is due to a limitation of the free rotation of the singly-linked carbon atoms. Generally free rotation occurs until the configuration, in which the system has the "maximum entropy" is attained. When there is little difference in the entropy between two or more of the possible configurations, then these forms may exist, and, moreover, be interconvertible by feeble chemical agencies if the difference in entropy is sufficiently small.

The great difficulties of the investigation of the isomerism of the 1:3-diketones are emphasised by the recent researches on ethyl formylphenylacetate.[48] Until recently, this compound was supposed to exist in four different forms, two of which were possibly stereoisomerides. Michael's reinvestigation (*loc. cit.*) has led him to the conclusion that there are only three forms, one liquid and

[47] *Annalen*, 1912, **390**, 30; *A.*, i, 631.

[48] W. Wislicenus, *ibid.*, **389**, 265; *A.*, i, 624; A. Michael, *ibid.*, **391**, 235, 275; *A.*, i, 861; K. H. Meyer, *Ber.*, 1912, **45**, 2843; *A.*, i, 940.

two solid, all of which are, however, enolides. Wislicenus (*loc. cit.*), on the other hand, has reduced the number to two, the liquid ester (α), the hydroxymethylene (I), and the crystalline γ-form (m. p. 110°), which is considered to be the enol-aldo-form (II), owing to its reaction with decolorised magenta:

$$\underset{\text{(I.)}}{OH\cdot CH{:}CPh\cdot CO_2Et} \qquad \underset{\text{(II.)}}{OCH\cdot CPh{:}C(OH)\cdot OEt} \qquad \underset{\text{(III.)}}{OCH\cdot CHPh\cdot CO_2Et}$$

The other forms are merely mixtures of these, whilst the true aldo-form (III) has not been isolated, but may be present in alcoholic solution. The method of bromination, however, seems to offer a ready way of solving the problem. The liquid α-form, and the liquid obtained by melting any of the so-called solid forms, are, as usual, an equilibrium mixture, containing about 76 per cent. of enolide, probably both (I) and (II); the γ-form (m. p. 110°) is a pure enolide, as is also the β-form (m. p. 50°). One of these, most probably the γ-ester, is the hydroxymethylene (I). All solutions contain the true aldo-form in equilibrium with enolides; in 50 per cent. methyl alcohol as much as 91 per cent. of the ester is the aldehyde.

Metallic Derivatives.—Although there seems clear evidence that most metallic derivatives of 1 : 3-diketones and such-like compounds are salts of the enolides, the mercury compounds seem uniformly to be derivatives of the ketones; in fact, in the case of some bis- and tris-indandiones, these salts are the only representatives of the ketonic form.[49] The various formulæ given in the literature show that some uncertainty still exists as to the constitution of the metallic derivatives of compounds of the malonic ester type. Although this type reacts in the same manner as the 1 : 3-diketones, no enolide can be discovered either in the liquids or in solutions by the methods described in the foregoing. That the relation:

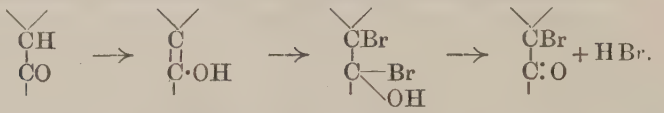
$$\cdot CH\cdot CO\cdot OR \rightleftarrows C{:}C(OH)\cdot OR$$

does hold, and that the metallic derivatives are salts of the enolide, can be readily demonstrated by the bromination method, for on adding a solution in alcoholic sodium methoxide to an acidified bromine solution, as much as 90 per cent. of the compound appears as enolide. The interval of one minute is, however, sufficient for the entire disappearance of the enolide.[50]

Bromination of Desmotropic Compounds.—Since Lapworth[51] originally demonstrated that the bromination of compounds containing the carbonyl group (ketones, acids, etc.) must be a reaction between bromine and an enolic form, as the speed of the reaction is independent of the concentration of the bromine, and hence most probably fixed by some slow change of the ketonic into the enolic form, little

[49] Hantzsch, *loc. cit.* [50] K. H. Meyer, *loc. cit.* [51] *T.*, 1904, **85**, 30.

has been added to our knowledge of the phenomena until Meyer's (*loc. cit.*) recent application of the process as a method of estimating the quantity of enolide in an equilibrium mixture, and the recent study of the speed of production of the chemical active form by means of its reaction with iodine.[52] This reaction of bromine with compounds containing this group is greatly accelerated by many catalysts (acids, bases, ferric chloride, etc.), but it offers a remarkable contrast to the action of chlorine and bromine on most other compounds, in that it is not accelerated by light.[53] This fact brings out clearly the difference between the direct substitution and the indirect substitution, which may be formulated thus:



Whether the Hell-Volhard reaction of bromine with acid chlorides, in which both hydrogen chloride as well as hydrogen bromide is eliminated, has a similar mechanism is doubtful, for hydrogen bromide and an acid chloride yield an acid bromide and hydrogen chloride.[54]

Of the many papers which deal directly or indirectly with the subject of this section, reference may be made to the study of the reaction of benzylamine on acetylacetone,[55] of the desmotropic alkyl derivatives of benzoylacetone,[56] and of the so-called "dibenzoylmethane," [57] and to the preparation of *C*- and *O*-alkyl derivatives in general of diketones or anilides.[58]

Quinones and Quinone-ammonium Compounds.

Quinone-ammonium Compounds.—One of the most interesting discoveries of the year is that of the quinone-ammonium compounds [59] obtained by the extreme methylation of picramic and *iso*picramic acids by methyl sulphate. Three methyl groups become attached to the acid, and there is no doubt that they are combined with the nitrogen, for the derivatives from *iso*picramic acid is isomeric with dinitrodimethyl-*p*-anisidine,[60] and secondly, demethyla-

[52] H. M. Dawson and F. Powis, *T.*, 1912, **101**, 1503.

[53] K. H. Meyer, *Ber.*, 1912, **45**, 2867; *A.*, i, 941.

[54] O. Aschan, *Annalen*, 1912, **387**, 10; *A.*, i, 198; E. Mohr, *J. pr. Chem.*, 1912, [ii], **85**, 334; *A.*, i, 362.

[55] L. Rügheimer and G. Ritter, *Ber.*, 1912, **45**, 1332; *A.*, i, 474.

[56] W. Dieckmann, *ibid.*, 2685; *A.*, i, 868.

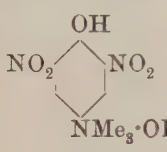
[57] R. D. Abell, *T.*, 1912, **101**, 989, 998.

[58] K. Auwers, *Ber.*, 1912, **45**, 976, 994; *A.*, i, 484, 486.

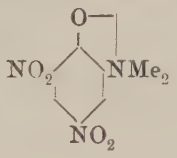
[59] R. Meldola and W. F. Hollely, *P.*, 1910, **26**, 232; *T.*, 1912, **101**, 912.

[60] F. Reverdin and A. de Luc, *J. pr. Chem.*, 1911, [ii], **84**, 555; *A.*, 1911, i, 965.

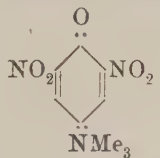
tion can only be effected by vigorous treatment, which would not be the case if one methyl group were attached to a nitro-group. These quaternary bases both have an ochreous colour, but the *p*-derivative combines with water, forming bright red crystals. The salts, however, are colourless, and very readily hydrolysed. The compounds are not phenolic, and have not been acylated. The remarkable colour is confined to the nitro-compounds, for the corresponding trimethyl derivatives of *p*-aminophenol and of 2 : 6-dibromo-*p*-aminophenol are colourless. The exact constitution of the bases is not an easy matter to determine. The colourless salts seem obviously derivatives of dinitrohydroxyphenyltrimethylammonium hydroxide (I), but the colour of the anhydrous bases suggests some deeper constitutional change than a simple elimination of water (II). The quinonoid (III) structure, alone, necessitates the use of the very unusual linking of quinquevalent nitrogen entirely to



(I.)



(II.)



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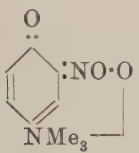

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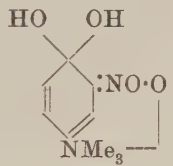
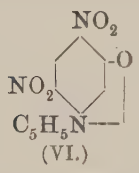


(V.)

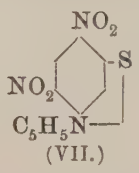
carbon. A quinonoid formula (IV), in which an *aci*-nitro-group is linked to the quaternary nitrogen, would not be open to this objection, and also would account for the fact that only the nitro-derivatives are coloured. The constitution of the red "hydrate" of the *p*-compound is yet more of a puzzle. If the ochreous anhydrous bases are "inner" salts, it would seem necessary that the neutral hydrate should also have that structure; then the disposal of the hydrate water (hydroxyl group) is most simply arranged for by a quinole formula (V). The fact that this compound has an intense colour, whilst all known quinoles, none of which are, however, nitrated, are colourless, is not a special difficulty, since the cause of the colour of the "hydrate," as well as of the anhydrous base, may lie in the formation of the "inner" salt. The attachment of two hydroxyl groups to the same carbon atom is not without analogy, when the carbon atom bears the same relation as is found here, to negative groups (for example, mesoxalic acid). The adherents of the subsidiary valence hypo-

thesis, which has not been called into use by the authors, should find no difficulty in constructing a formula which would account for the exact tint. The properties of these quinone-ammonium compounds are strongly reminiscent of the quinonediazides, of which the anthraquinone derivatives are now known.[61] The latter are invariably coloured, but form *colourless* salts, which are very extensively hydrolysed. Assuming the absence of colour in the salts to be due to their benzenoid diazonium structure, $HO{\cdot}C_6H_4{\cdot}N_2{\cdot}X$, it is difficult to understand the extensive hydrolysis. A remarkable example[62] of an analogous phenomenon has recently been observed in 4′-hydroxy-4-diazodiphenyl,

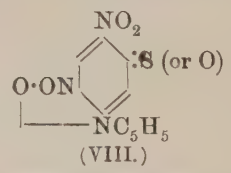
the highly unstable diazophenol is deeply coloured, and yields pale yellow, hydrolysable salts, which, however, form ruby-red hydrates (with $2H_2O$). It is probable that similar constitutional changes are the origin of these properties. Still more striking is the similarity between the nitroquinone-ammonium compounds and the dinitrophenylpyridinium compounds.[63] An oxygen compound and the sulphur compound, to which the formulæ (VI) and (VII) are



(VI.)



(VII.)



(VIII.)

given, are both coloured, but form colourless, hydrolysable salts. The sulphur compound, moreover, forms a hydrate, which is far more deeply coloured. From the resemblance to the quinone-ammonium compounds, it might be suggested, since the pyridine ring is not opened, that the free base is a quinonoid "inner" salt (VIII), the colourless salts benzenoid, and the coloured hydrate of the quinole type. Since in this case the nitrogen and oxygen (or sulphur) are not respectively para or ortho to one another, and yet all the same properties are observed, the quinonoid "inner salt" structure for the free base seems the more probable. The constitution of the coloured "hydrates" which may be quinoles (or, it may be suggested, possibly compounds of quinhydrone type, which would harmonise with the intensified colour) is more

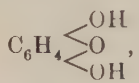
[61] R. Scholl, F. Eberle, and W. Tritsch, *Monatsh.*, 1911, **32**, 1043; *A.*, i, 143.

[62] E. Bamberger, *Annalen*, 1912, **390**, 131; *A.*, i, 691.

[63] F. Reitzenstein and J. Rothschild, *J. pr. Chem.*, 1906, [ii], **73**, 257; *A.*, 1906, i, 454; T. Zincke and G. Weisspfenning, *J. pr. Chem.*, 1910, [ii], **82**, 1; *ibid.*, 1912, [ii], **85**, 211; *A.*, 1910, i, 585; 1912, i, 302.

uncertain; it is significant that neither have hydroxyl groups been recognised, nor the molecular weights determined.

o-Benzoquinones.—A large number of derivatives or homologues of *o*-benzoquinone have now been prepared, but the colourless form,[64] in which the parent substance was originally obtained, has only been once again observed (3 : 4-toluquinone). Kehrmann[65] urges that there is as yet not even sufficient evidence to conclude that the two forms are isomeric, much less desmotropic, and suggests that the colourless compound is possibly the first phase in the oxidation of catechol, thus:

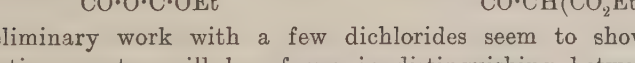


or even a compound of the quinone with ether.

Besides the study of many reactions of the quinones, a very large amount of preparative work is being done in the anthracene, phenanthrene, and other series of quinones or quinonoid compounds, of which this indication must suffice.

Some Phthalyl Derivatives.

Phthalyl Chloride.—The evidence on which the asymmetric constitution of phthalyl chloride rests has been again examined in detail,[66] with the result that the symmetric formula is favoured. The proximity of the ·COCl-groups in phthalyl chloride is considered as sufficient cause for such reactions as that with ammonia, in which *o*-cyanobenzoic acid is formed, instead of a diamide. The reactions with ethyl sodiomalonate and sodioacetate supply the chief grounds for this opinion, since, for example, the constitutions of the two malonic compounds are best expressed by the formulæ:



Preliminary work with a few dichlorides seem to show that absorption spectra will be of use in distinguishing between the two types of constitution of this and similar dichlorides. This view has found definite proof in Ott's[67] elaborate investigation of certain acid chlorides of dibasic acids, which mainly deals with the constitution of maleic and fumaric dichlorides. As criteria to distinguish between the lactonic and the symmetric formulæ, the

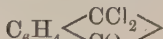
[64] R. Willstätter and others, *Ber.*, 1911, **44**, 2171, 2182; *A.*, 1911, i, 728, 729; C. L. Jackson and G. L. Kelley, *Amer. Chem. J.*, 1912, **47**, 197; *A.*, i, 275.

[65] *Ber.*, 1911, **44**, 2632; *A.*, 1911, i, 883.

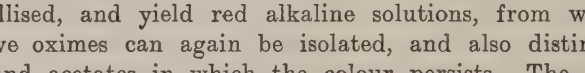
[66] Scheiber, *Annalen*, 1912, **389**, 121; *A.*, i, 559; *Ber.*, 1912, **45**, 2252; *A.*, i, 701.

[67] *Annalen*, 1912, **392**, 245; *A.*, i, 828.

rates of reaction with aniline and methyl alcohol are taken, as well as the molecular volume, which is known to drop by about four units in the formation of a lactone ring. Both these tests indicate that ordinary phthalyl chloride is symmetrically constituted. Further, the author has been able to convert phthalyl chloride by heating with aluminium chloride into an isomeride, a crystalline solid, melting at 88—89°. By distillation, prolonged heating at 100°, or in the presence of hydrogen chloride, it is reconverted into the ordinary chloride. It reacts with aniline and methyl alcohol far more slowly than the ordinary chloride, and is taken to be the asymmetric chloride:



The interaction of phthalic anhydride and hydroxylamine yields two isomeric oximes,[68] one colourless and the other yellow, which are mutually convertible the one into the other. Both can be recrystallised, and yield red alkaline solutions, from which the respective oximes can again be isolated, and also distinct ethyl ethers and acetates in which the colour persists. The colour is due mostly, if not entirely, to fluorescence. The evidence seems in favour of stereoisomeric formulæ:



As a contrast to these observations, the two differently coloured varieties of phthalylhydrazides, which are normal and not *iso*-compounds, have been shown to be polymorphs, and not isomerides.[69]

The chromoisomerism exhibited by a number of imides and amides of dibasic acids has been investigated by means of the absorption spectra of solutions. The identity of the spectra of differently coloured solid forms is taken to indicate the absence of chemical isomerism. Thus, on this criterion, the yellow and white forms of *p*-methoxyphenylphthalimide are not chemical isomerides, whilst *p*-methoxy- and *p*-ethoxy-phenylmaleinimides, and the corresponding phenylfumardiamides, each of which exist in two forms, are.[70]

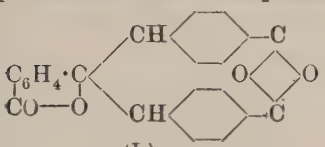
[68] W. R. Orndorff and D. S. Pratt, *Amer. Chem. J.*, 1912, **47**, 89. Compare Lassar-Cohn, *Annalen*, 1880, **205**, 295 ; *A.*, 1881, 585, and R. Meyer and S. M. Kissin, *Ber.*, 1909, **42**, 2825 ; *A.*, 1909, i, 652.

[69] F. D. Chattaway and D. F. S. Wünsch, *T.*, 1911, **99**, 2253.

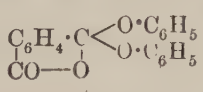
[70] A. Piutti and E. de'Conno, *Mem. R. Accad. Lincei*, 1911, [v], **8**, 793 ; *A.*, i, 360 ; compare Piutti and Calcagni, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 255 ; *A.*, 1911, i, 124.

Benzeins and Phthaleins.

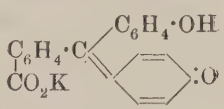
Phenolphthalein.—Although there has been much discussion as to the constitution of the salts of phenol- and other phthaleins,[71] which cannot be considered as final, the formula of the phthaleins themselves has not been called in question, but von Baeyer's formula generally accepted. When tested by the very striking way of ascertaining the presence of "active" hydrogen (hydrogen linked to oxygen, nitrogen, sulphur), which has been devised by B. Oddo[72] on the basis of Sudborough and Hibbert's[73] original use of Grignard's reagent for estimating hydroxy- and amino-groups, phenolphthalein does not appear to contain an active hydrogen atom.[74] Moreover, it should be noted that throughout the phthalein series the carbonyl group of the lactone ring is indifferent to Grignard's reagent, with which phenolphthalein does not react. On the other hand, one active hydrogen is found in the monopotassium salt, the iminophenolphthalein, and in the diacetyl, but none in the triacetyl derivative. In fluorescein, however, two active hydrogen atoms are indicated. Since the usual formula for phenolphthalein, as well as that for fluorescein, shows two hydroxyl groups, it is argued that the former requires modification. The formula (I) is suggested, which represents the compound as having an ether-like constitution, but it is hinted that a still more revolutionary formula (II) may represent free phenolphthalein. The monopotassium salt (III) would still be repre-



(I.)



(II.)



(III.)

sented by the quinonoid formula most generally accepted. The cause of the different structures of phenolphthalein and fluorescein is sought in the fact that in the latter the benzene nuclei carrying the hydroxyl groups become fixed by the formation of the anhydride, whereas in the former free rotation is possible, and the most stable arrangement is found in the formula (I) suggested.

Recent work on the use of phenolphthalein and its derivatives as indicators[75] brings out the fact that the presence of negative

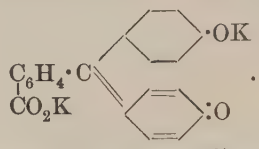
[71] *Ann. Report*, 1909, 66. [72] *Ber.*, 1911, **44**, 2048; *A.*, 1911, ii, 826.

[73] *T.*, 1904, **85**, 933; *ibid.*, 1909, **95**, 477; Th. Zerewitinoff, *Ber.*, 1907, **40**, 2023; 1908, **41**, 2233; 1912, **45**, 2384; *A.*, 1907, ii, 509; 1908, i, 93; 1912, i, 841.

[74] B. Oddo and E. Vassallo, *Gazzetta*, 1912, **42**, ii, 204; *A.*, i, 792.

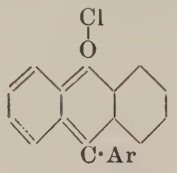
[75] E. Rupp, *Arch. Pharm.*, 1911, **249**, 56; *A.*, 1911, i, 301; J. W. McBain, *T.*, 1912, **101**, 814.

groups in the phthalein nucleus, but not in the phenol nuclei, sharpens the colour change, that is, increases the rapidity of the formation of the coloured quinonoid form, and hence increases the value of the phenolphthalein as an indicator. The preparation of colourless monobasic and tribasic salts[76] from phenolphthalein, which contain water or alcohol, may perhaps be taken as evidence that only the formation of the dibasic salts causes the development of the colour, thus:



Phthaleins and Benzeins.—The complicated isomerism in the phthaleins and benzeins has been accounted for by F. Kehrmann and others[77] by constitutional formulæ showing quadrivalent oxygen; the salts with acids are held to be, on the one hand, oxonium salts (I), or, on the other hand, from the similarity with the salts of triphenylmethyl, generally carbonium salts,[78] (II), thus, in typical formulæ:

(I.)



(II.) $C_6H_4<^{CPh:}_{O-\!-}$ $<^{H}_{Cl}$

A new light has, however, been thrown on the problem by von Liebig's[79] final demonstration that some, if not all, of the isomerides are, in fact, easily resolvable polymerides, the correct molecular weight of which is only found in certain solvents (acetone); the polymerides are, however, sufficiently stable to yield salts and other derivatives. In the formulæ of these compounds oxygen is not represented as quadrivalent, but the author is obliged to fall back upon limitations to the free rotation of the phenyl groups, about the central methane carbon atom, to which they are singly linked, in order to account for the existence of the certain isomeric unimolecular fluoresceins. The polymerides are considered to be of a quinhydrone type, and analogous to the

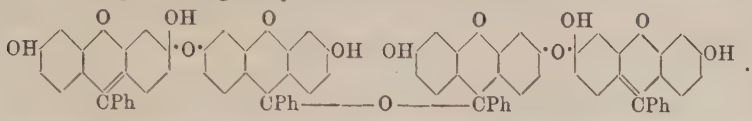
[76] P. A. Kober, and J. T. Marshall, *J. Amer. Chem. Soc.*, 1911, **33**, 59; 1912, **34**, 1424; *A.*, 1911, i, 300; 1912, i, 865; R. Meyer and F. Posner, *Ber.*, 1911, **44**, 1954; *A.*, 1911, i, 654.

[77] *A.*, 1900, i, 61; *Annalen*, 1910, **372**, 287; *A.*, 1910, i, 406; *Ber.*, 1912, **45**, 3346, 3504; *A.*, i, 1012.

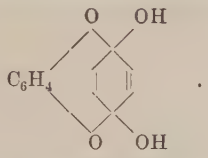
[78] M. Gomberg and collaborators, *Annalen*, 1909, **370**, 142; *A.*, 1910, i, 55; *J. Amer. Chem. Soc.*, 1911, **33**, 1211; *A.*, 1911, i, 737.

[79] H. von Liebig, *J. pr. Chem.*, 1912, [ii], **85**, 97, 241; **86**, 472; *A.*, i, 376.

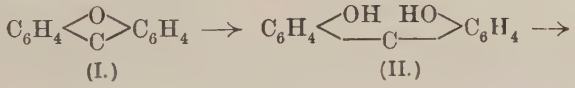
compounds of benzeins with alcohol and other hydroxy-compounds. Thus, γ-resorcinolbenzein, $4C_{19}H_{12}O_3,H_2O$, which only loses water at 240°, is given a quinhydrone formula:



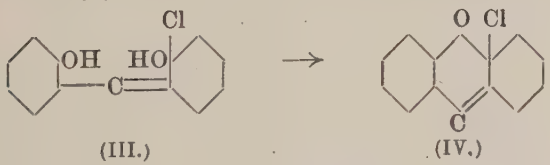
As will be seen from the formulæ, these quinhydrones are represented by definite structural formulæ, with full atomic linkings; in fact, in discarding subsidiary linkings, the author is reverting to C. L. Jackson's original formula for quinhydrone [80]:



The salts with acids are not regarded as oxonium nor as carbonium derivatives, although the acid radicle is attached to carbon (IV), but as compounds of the quinhydrone type. It is admitted that the solubility in water of these salts is a difficulty, but it is suggested that in solution they are represented by (III). Basing his conception on von Baeyer's [81] recent discoveries on the method of opening up the dimethylpyrone ring, the author considers that the formation both of the salts and of the quinhydrone additive compounds is brought about by the hydrolysis of the anhydride ring; the varying, so-called, "basicity" of this class, which is admittedly not commensurate, as is usual, with the character of the substituents, is merely a question of the readiness with which this hydrolysis occurs:



(I.) (II.)



(III.) (IV.)

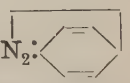
Diazo-compounds.

The data of the absorption spectra of a large number of diazo-compounds of various types which have been accumulated by several observers make it now possible to associate the constitutions

[80] *Ber.*, 1895, **28**, 1614; *A.*, 1895, *A.*, i, 513.
[81] *Annalen*, 1911, **384**, 208; *A.*, 1911, i, 901.

of the different classes with certain characteristics of the spectra, and to state the modifications in the typical spectra produced by the presence of certain groups or radicles. Moreover, by this means the current conceptions as to the constitution of many diazo-compounds can be checked, or in some cases corrected.[82]

The diazo-compounds are by their absorption spectra divided into two groups, the diazonium salts and the azo-compounds. The diazonium derivatives possess a characteristic deep band in the ultra-violet, the exact position and intensity of which is modified by, but the character of which remains unchanged by, substituents. The coloured and colourless salts are quite similar in this respect, and hence have the same constitution, a view which is now held by G. T. Morgan,[83] on the ground of chemical behaviour. This powerful selective absorption is attributed by Hantzsch to the interaction between two "unsaturated centres,"[84] which produces a peculiar vibratory molecular state. He represents it by ancillary linking or subsidiary valence. In this case the tervalent nitrogen of the diazo-group is linked to the benzene nucleus by such a valence, thus: Ar–N–X. This structure is, however, not the same

as, or even similar to, Cain's[85] quinonoid diazo-formula, 

for the nucleus is supposed to retain its benzenoid type, and no nitrogen-bridge linking to be formed. It is pointed out that the so-called diazo-phenols show a very different and characteristic absorption, which is taken to indicate that they have a quinonoid structure, not a benzenoid with a bridge linking, a formula which

has again recently found adherents. At the same time this difference in the absorption between the two types is an argument for the benzenoid structure of the diazonium salts.

The spectra of the azo-compounds is quite different from that of the diazonium salts, and is, moreover, extremely variable. The azo-group does not appear to be an "independent" chromophore, but resembles the carbonyl, only to a higher degree, in its dependence on the groups to which it is linked. The azo-paraffins have an ultraviolet absorption band, and the azo-benzenes have, in addition, a "colour" band in the visible spectrum. From the great

[82] A. Hantzsch and I. Lifschitz, *Ber.*, 1912, **45**, 3011; *A.*, ii, 1116.
[83] *T.*, 1910, **97**, 1961, 2537; compare *ibid.*, 1907, **91**, 1311.
[84] See also A. K. Macbeth, A. W. Stewart, and R. Wright, *T.*, 1912, **101**, 599.
[85] *T.*, 1907, **91**, 1069.

similarity of the diazomethane derivatives to azo-compounds, the cyclic formula for the group $>C<^{N}_{N}$ is preferred to the formula $>C{:}N{:}N$, suggested by Angeli and Thiele.[86]

The isomeric azocyanides, $Ar{\cdot}N_2{\cdot}CN$, and azosulphonates,[87] $Ar{\cdot}N_2{\cdot}SO_3M{\cdot}$, behave as stereoisomerides, showing a nearly identical absorption. The two series of diazotates show, however, considerable difference, the normal or "*syn*"-salts showing no ultra-violet band. Further, it is to be noted that faintly alkaline solutions of diazonium salts in which it has been asserted that the diazohydrate (normal) is present, are now shown by the absorption to contain the diazonium hydroxide. This fact suggests that the conversion of the diazonium into the diazo-constitution which was offered as an explanation of many diazo-reactions (transformation into phenol, chlorobenzene, etc.), does not at least find confirmation in this searching analytic method. The free *iso*(*anti*-) diazohydrate can be obtained in solution, showing absorption identical with that of its salts, but quite different from that of the nitrosoamines, the absorption of which resembles rather that of the normal diazotates. The opinion is expressed, however, that the normal and *iso*diazotates are stereoisomerides, and that the difference in the spectra is to be attributed to the peculiar chromophoric character of the azo-group. It will be seen, however, that it is just where a decisive proof was most needed that some uncertainty still remains.

The evidence for the existence of the primary nitrosoamines as the ψ-acids of the *iso*diazotates, $Ar{\cdot}N{:}N{\cdot}OM \rightleftarrows Ar{\cdot}NH{\cdot}NO{\cdot}$, has again been examined, more particularly in the case of *p*-nitrodiazobenzene, and a remarkable effect of solvents discovered. In ether (or alcohol) the absorption is that of an *iso*diazotate, but in chloroform that of a nitrosoamine; moreover, the compound cannot be extracted from the latter solution by alkali, but only after addition of ether.[88] Although the absence of any equilibrium mixture in solution is very singular, if not unique, the reciprocal conversion of one isomeride to the other seems to take place with the rapidity which would be expected of such a change.

Some Reactions of Diazo-compounds.—The actions of sodium arsenite and a mixture of potassium cyanide and sodium hydrogen sulphide afford unusually clear chemical distinctions between the

[86] *Atti R. Accad. Lincei*, 1911, [v], **20**, i, 625; *A.*, 1911, i, 620; *Ber.*, 1911, **44**, 2522, 3336; *A.*, 1911, i, 845; 1912, i, 16.

[87] J. J. Dobbie and C. K. Tinkler, *T.*, 1905, **87**, 273. *Private communications* from C. H. Desch.

[88] E. Bamberger and O. Baudisch, *Ber.*, 1912, **45**, 2054; *A.*, i, 733; A. Hantzsch, *ibid.*, 3036; *A.*, i, 1039.

various classes of diazo-compounds. With diazonium salts, the normal diazotates, and the labile diazosulphonates, the diazo-group is replaced by hydrogen:

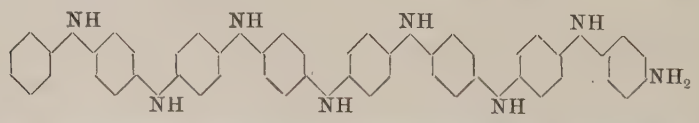
$$Ar{\cdot}N{:}N{\cdot}ONa + Na_3AsO_3 + H_2O = ArH + N_2 + Na_3AsO_4 + NaOH$$
$$Ar{\cdot}N{:}N{\cdot}ONa + NaSH + KCN + H_2O = ArH + N_2 + KCNS + 2NaOH,$$

whilst the *iso*diazotates, the stable diazosulphonates, and azo- and azoxy-compounds do not react. A constitutional difference for the two sulphonates, $Ar{\cdot}N_2{\cdot}O{\cdot}SO_2K$ and $Ar{\cdot}N_2{\cdot}SO_3K$, is revived to account for this distinct reactivity; and azo-formulæ are suggested for nitrosoacet- and nitrosobenz-anilides, $Ar{\cdot}N_2{\cdot}O{\cdot}Ac$, since they react whilst the nitroso-derivatives of amines do not.[89]

Two of the simplest derivatives of azo-benzene, *o*-hydroxy-[90] and *o*-amino-azobenzene[91] have been prepared by convenient methods; the former is obtained by coupling diazonium salts with *p*-acetyl-aminophenol, and the latter, of which derivatives have also been obtained,[92] by condensing benzoyl-*p*-phenylenediamine with nitroso-benzene.

Aniline-black and Allied Compounds.

Since aniline-black was last dealt with in the Annual Reports (1909), the two chemists who are authorities on this subject, Green and Willstätter,[93] have maintained a long controversy as to the exact nature and relations of aniline-black, or perhaps more accurately, of the primary products of the oxidation in which aniline-black is ultimately formed. Since Willstätter's discovery[94] that one-eighth of the nitrogen appears as ammonia on treatment of any of the products with acids, it has been generally agreed that an octa-nuclear indamine-like complex is the parent substance, the leuco-form of which ("leucoemeraldine"), $C_{48}H_{42}N_8$, is represented by the annexed formula:



The four coloured compounds derived from this contain respectively one, two, three, and four quinonoid nuclei. Inasmuch as all

[89] A. Gutmann, *Ber.*, 1912, **45**, 821; *A.*, i, 398.

[90] J. T. Hewitt and W. H. Ratcliffe, *T.*, 1912, **101**, 1765; N. N. Voroschtsoff, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 787; *A.*, 1911, i, 818.

[91] F. H. Witt, *Ber.*, 1912, **45**, 2380; *A.*, i, 921.

[92] G. M. Norman, *T.*, 1912, **101**, 1913.

[93] R. Willstätter and C. Cramer, *Ber.*, 1910, **43**, 2976; *A.*, 1911, i, 90; *Ber.*, 1911, **44**, 2162; *A.*, 1911, i, 736; A. G. Green and A. E. Woodhead, *T.*, 1910, **97**, 2388; 1912, **101**, 1171; *Ber.*, 1912, **45**, 1955; A. G. Green and S. Wolff, *Ber.*, 1911, **44**, 2570; *A.*, 1911, i, 900.

[94] *Ber.*, 1909, **42**, 2147, 4118; *A.*, 1909, i, 535, 975.

these compounds are unstable and amorphous, and cannot be purified by recrystallisation, the difficulties experienced in demonstrating, much more in defining, these stages, has been very great. Willstätter relied on the quantitative reduction with the evolution of nitrogen of the quinonoid nucleus by phenylhydrazine as a means of measurement; but Green has shown that although accurate within certain limits of temperature, 80—90°, phenylhydrazine itself decomposes rapidly at the temperatures which were used; hence the conclusions were falsified. On the other hand, the oxidation of titanium chloride appears to be a more trustworthy guide; it reduces each of the quinonoids to the leuco-compound, and not merely to the monoquinonoid stage as was first believed.

The colour-bases are all completely soluble in 80 per cent. acetic acid; their salts, with the rise in the number of quinonoid nuclei, are respectively grass-green, green, blue, and purple. The names proto-emeraldine, emeraldine, nigraniline, and pernigraniline are suggested for the four stages in oxidation. These compounds are unstable, and pernigraniline especially readily becomes degraded to a lower quinonoid stage. In attempts to purify, treatment with powerful reagents, strong acids, cause, besides degradation; the formation of insoluble compounds. This instability, as well as the colour, indicates that none of these compounds is aniline-black; they are rather to be regarded as intermediaries in its formation. It may be suggested that aniline-black is a quinhydrone-like complex of one or more of them.

Triphenylmethane Dyes and Triphenylmethyl.

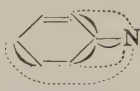
The discussions on the constitution of this group of compounds is so closely connected with the problem of the relation between colour and constitution that the recent evolution of ideas on this subject will have to be mentioned.

H. Kauffmann has recently developed in a monograph[95] views as to the interatomic linkings in aromatic (and other) compounds, which are suggested by their varying behaviour in a Tesla electric field.[96] He regards the benzene nucleus as a structure in which the interatomic relations are most delicately balanced, and hence highly sensitive to the influences of substituents. In this way groups act as auxochromes in varying degrees by causing changes in the chromophoric aromatic nucleus, with consequent changes in the absorption of light (Kauffmann's "Auxochrome theory"). These changes are not, however, the simple conversion from the benzenoid to the quinonoid structure, but they are at once more varied and

[95] "Die Valenzlehre," 1911; *Ber.*, 1912, **45**, 766, 781; *A.*, i, 351, 397.

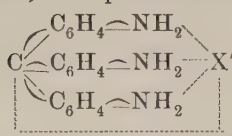
[96] *Ber.*, 1900, **33**, 1725; 1901, **34**, 682; *A.*, 1900, i, 480; 1901, i, 318.

more complex; thus in order to show the influence of a substituent on the nuclear structure, he represents dimethylaniline by the formula:

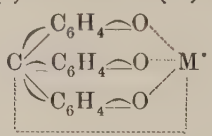


in which the substituent is connected with four of the carbon atoms of the nucleus. The collection of the sub-valencies on certain atoms is looked upon as determining the well-known direction given to a second substituting group.

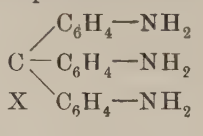
It is in particular in this extreme division of the valence unit ("Valenzzersplitterung"), brought about by auxochromic groups (which is at least in part merely an extension of the use of subsidiary valencies), that the author sees the cause of colour. Attention has been called to the fact that auxochromes are not, as might be expected on this theory, always similarly effective; the action holds for the aromatic series, but in the aliphatic these groups rather decrease selective absorption.[97] The particular application to the triphenylmethane dyes well illustrates Kauffmann's views; thus pararosaniline (I) and aurin (II) are represented thus:



(I.)



(II.)



(III.)

The single valence-unit of the anion is divided in this case into four parts, which are not necessarily equal, but determined by the strength of the auxochromic group; in the breaking up of the four valence-units of the central carbon atom lies the cause of the colour. The three benzene rings are exactly alike and each modified to an equal extent, whereas in Fittig's formula one only is quinonoid, and on von Baeyer's theory[98] each is successively quinonoid in the vibratory movement of the molecule, to which the colour is ascribed. One of the difficulties of the usual quinonoid formula is the fact that the salts of pararosaniline are not hydrolysed, whilst in general the salts of such ψ-bases containing the carbimine chromophore, ·C:NH,HCl, are highly unstable. Again this theory easily represents the fact that on weakening the auxochromic groups (by acetylation) the colour fades, and the molecule may be supposed to pass over finally into Rosenstiehl's formula (III).[99]

[97] A. Hantzsch, *Ber.*, 1912, **45**, 3036; *A.*, ii, 1116.

[98] *Annalen*, 1907, **354**, 164; *A.*, 1907, i, 757.

[99] *Compt. rend.*, 1895, **120**, 192, 264, 331, 740; *Bull. Soc. chim.*, 1895, [iii], **13**, 427, 431; *A.*, 1895, i, 377, 476, 667.

The intense halochromy of hexamethoxytriphenylcarbinol and even of hexamethoxytriphenylmethane, would be anticipated from the great auxochromic subdivision of the carbon valence.[1]

As a result of his study of the coloured compounds of metallic salts, mainly tin tetrachloride, with the carbonyl group, Pfeiffer[2] has arrived at somewhat similar views as to the development of colour. In these compounds the metallic salt or acid (called the "addendum") unites "co-ordinatively" at the carbonyl oxygen, $X_4Sn<^{O:CRR'}_{O:CRR'}$, thereby neutralising free affinity and rendering the carbonyl carbon more unsaturated. The appearance of unsaturation is the cause, the degree determining the intensity of colour. Hence it must depend both on the addendum and on the nature of the groups R and R′. A very large body of facts has been gathered together, which affords a remarkable confirmation of this proposition. According to Kauffmann's theory, the addendum would be united both to the carbon and oxygen (and to other points in the groups R and R′, or to any auxochromic groups), and the consequent breaking up of the carbon valence, which, it must be remembered, also occurs in the increase of "unsaturation" of Pfeiffer, gives rise to colour. The hypothesis of Pfeiffer has the advantage in that these additive compounds are, in fact, more, not less, reactive, and hence more unsaturated than the original carbonyl derivatives; thus the catalytic hydrolysis of an ester by an acid is accounted for by the attachment of water to the carbonyl carbon, thus:

$$R{-}\overset{\displaystyle OEt}{\underset{\displaystyle H_2O}{\overset{|}{\underset{:}{C}}}}{:}O{\cdots}H^{\cdot}\ ,$$

Moreover, when such a "ternary" compound can be produced, and the unsaturation of the carbon atom thereby diminished, it is found that the colour fades. This theory can be used as Kauffmann's to account for the colour of the triphenylmethane dyes, without the assumption of the change of a benzenoid to a quinonoid nucleus, and of triphenylmethyl and the corresponding carbinol salts.

Triphenylmethyl.—Schlenk's[3] discovery of the unimolecular deeply-coloured tridiphenylmethyl, $(Ph{\cdot}C_6H_4)_3C$, supported by J. Piccard's[4] demonstration that the yellow colour of a solution of

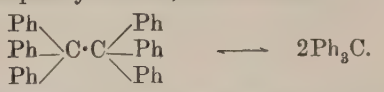
[1] H. Kauffmann and F. Kieser, *Ber.*, 1912, **45**, 2333; *A.*, i, 853.

[2] P. Pfeiffer, *Annalen*, 1910, **376**, 285; 1911, **383**, 92; *A.*, 1910, i, 852; 1911, i, 788.

[3] *Annalen*, 1910, **372**, 1; *A.*, 1910, i, 236.

[4] *Ibid.*, 1911, **381**, 347; *A.*, 1911, ii, 561.

triphenylmethyl in absolute ether increased on dilution, has confirmed the suggestion[5] that the coloured (solutions) and colourless forms of the latter are simply the coloured triphenylmethyl and the colourless hexaphenylethane, which exist in the equilibrium:



The colour is therefore not to be ascribed to the presence of a quinonoid nucleus in a coloured bimolecular form, the ionisation of which in solution (sulphur dioxide) into quinonoid and benzenoid triphenylmethyl is regarded by Gomberg[6] as the

cause of the conductivity. On Pfeiffer's hypothesis the colour is merely caused by the unsaturation of the methyl carbon atom. In an equally simple manner the appearance of colour in the triarylmethyl salts (for example, triphenyl- or trianisole-methyl chloride) in acid solution, or when combined with metallic salts or acids, is attributed to the decrease in the saturation of the central carbon atom, and not to the constitutional change which is shown in Gomberg's carbonium formula, $Ph_2C{:}C_6H_4{<}^{H}_{Cl}$. A remarkable difference[7] has been found to exist between the absorption spectra of the coloured non-conducting solutions of triphenylmethyl and of the conducting triphenylcarbinol or triphenylmethyl derivatives (salts); apparently the ion, $Ph_3C^{\cdot}$, has a characteristic spectrum. Whether these facts can be harmonised with the above views remains to be seen. The authors regard this contrast, not as indicating a constitutional change, but as being in favour of von Baeyer's[8] suggestion of a special ionisable carbonium valence, represented thus: $Ph_3C \frown X$, in the triphenylmethane salts.

The discovery of two isomeric tridiphenylcarbinols,

$$(C_6H_5{\cdot}C_6H_4)_3C{\cdot}OH,$$

and coloured unimolecular tridiphenylmethyls, respectively prepared from them, does not simplify the problem; once more the only suggestion offered is that one isomeride has an ionisable carbonium valence, whilst the other has not.[9]

The simple amine bases of the triphenylmethane series,

[5] J. Schmidlin, *Ber.*, 1908, **41**, 2471; *A.*, 1908, i, 623.

[6] M. Gomberg and collaborators, *ibid.*, 1907, **40**, 1847; *A.*, 1907, i, 504; *ibid.*, 1909, **42**, 406; *A.*, 1909, i, 144; *J. Amer. Chem. Soc.*, 1911, **33**, 531, 1211; *A.*, 1911, i, 361, 737.

[7] K. H. Meyer and H. Wieland, *ibid.*, 1911, **44**, 2557; *A.*, 1911, ii, 952.

[8] *Ber.*, 1905, **38**, 572; *A.*, 1905, i, 281.

[9] J. Schmidlin, *ibid.*, 1912, **45**, 3171; *A.*, 1913, i, 32

$NH_2 \cdot CAr_3$, which have for the first time been prepared,[10] resemble the carbinols so closely that they have probably been often overlooked. With acids they yield dyes and an ammonium salt:

$$Ar_3C \cdot NH_2 + 2HCl \rightleftarrows Ar_3CCl + NH_4Cl,$$

but on making alkaline the triarylmethylamine is again obtained. With alcohols a carbinol ether is produced in a quantitative reaction, which can be used to estimate the amino-group:

$$R_3C \cdot NH_2 + EtOH = R_3C \cdot OEt + NH_3.$$

The auramines, $Ar_2C{:}NH$, which are very strong bases, offer a remarkable contrast in their stability to the triarylmethylamines.[11]

Fluorescence.

As an illustration of the general theory of fluorescence of organic compounds (the luminophore-fluorogen theory [12]), the influence of amino-groups as auxochromes (fluorogens) in fluorescence has been fully studied in the case of the methyl amino- and 2:5- and 2:6-diamino-terephthalates.[13] The displacement of the fluorescent band towards the red is most marked in the diamines, more especially when the amino-groups are in the para-position with respect to one another. On acetylation or benzoylation the weakening of the auxochrome causes a reverse movement of the band; that is, in terms of the theory, the connexion by means of subsidiary valence of the nucleus (the luminophore) with the amino-group (the auxochrome or fluorgene) is diminished. The investigation of the effect of numerous solvents on the fluorescence of these compounds makes clear the fact that the fluorescent colour exhibited by a given substance depends on the dissociating power of the solvent. The fluorescence is both intensified and of longer wavelength in alcohols and acetic acid, whilst the position of the band is either unchanged or even shifted towards the blue by chloroform, benzene, and hexane. These effects are, however, only marked when strong auxochromes are present. Carbon disulphide stands apart in nearly extinguishing all fluorescence. Among fluorescent compounds, methyl dimethylaminoterephthalate is also an exception in that it only shows fluorescence (blue) in inactive non-dissociating solvents—a property which has been used to show that tin tetraethide belongs to this class of solvent. The author merely states that all these new observations are in accord with his general theory of fluorescence.

[10] V. Villiger and E. Kopetschni, *Ber.*, 1912, **45**, 2910; *A.*, i, 1030.

[11] L. Semper, *Annalen*, 1911, **381**, 234; *A.*, 1911, i, 577.

[12] H. Kauffmann, *Ber.*, 1907, **40**, 838; *A.*, 1907, ii, 215. See also *Ann. Report*, 1907, 10.

[13] H. Kauffmann and L. Weissel, *Annalen*, 1912, **393**, 1; *A.*, i, 863.

The fact that (? 2:5-)dicyanodihydroxy-*p*-benzoquinone, which has recently been prepared by the action of alcoholic potassium cyanide on chloroanil,[14] is strongly fluorescent, is difficult to explain on Kauffmann's theory, as quinones are not luminescent, and hence not luminophores. It is suggested that in spite of the marked colour, the compound has a peroxide, and not the typical quinonoid structure.

An attempt[15] has been made this year to formulate a general molecular theory of fluorescence (and phosphorescence). It is assumed that a molecule, more especially a complex molecule, may exist in several states, in which the subsidiary valence is "satisfied" to different degrees. In the final stable state, the "residual affinity" reaches a minimum when the maximum satisfaction of the subsidiary valence with the consequent loss of free energy has been attained. From analogy this process is spoken of as the condensation of the lines of force which radiate from each atom as a centre. By the absorption of light, energy is provided for the "opening up" of the system. By the selective absorption of light of wave-length, λ_2, the stages 1 and 2 are brought into photodynamic equilibrium. In solution in a suitable solvent it is possible to produce the phase (3) with absorption of light, λ_3. Now it is conceived that the process $1 \longrightarrow 2$ brought about by the absorption of λ_2, must disturb the whole system, and as one of the possible vibrations of the system has a frequency corresponding with λ_3, so light of wave-length λ_3 will be emitted—and hence fluorescence. Very striking evidence is found in the fact that *o*-aminobenzaldehyde and other similar compounds absorb in alcoholic hydrochloric acid solution (that is, in the "opening up" $2 \longrightarrow 3$), light of the same wave-length as they emit as fluorescence in alcoholic solution. Moreover, it is suggested that the development of colour in concentrated sulphuric acid solutions of triphenylcarbinol may be accounted for in the same way, since the fluorescent light of the alcoholic solution is identical with the light absorbed in sulphuric acid solution, without resource to the hypothesis of a quinonoid structure. This suggestion as to the structure of these salts, it will be noted, is identical with that reached by Kauffmann and Pfeiffer on other grounds.

This theory has been effectively criticised from the point of view of the Mass Law.[16] It is urged that in any such system as postulated in the foregoing, there must be equilibrium between the various states, $1 \longleftrightarrows 2 \longleftrightarrows 3$, whether when constantly illuminated or not. Hence a "balance of light" would be attained in addition

[14] M. M. Richter, *Ber.*, 1911, **44**, 3469; *A.*, i, 34.

[15] E. C. C. Baly and R. Krulla, *T.*, 1912, **101**, 1469.

[16] A. K. Macbeth, *P.*, 1912, **28**, 271.

to the original absorption effect. The same argument may be applied to the absorption of each subsequent "state" which is induced in the system; but emission finds no place. The fluorescence which only occurs at low temperatures, and the fact that the wavelength of the exciting light may vary over a wide range without effecting that of the fluorescence, can also not be brought into accord with the theory.

Hydroaromatic Compounds, Terpenes, and Allied Compounds.

Physical Constants and Constitution.—The systematic study of physical constants has long been used as a supplementary guide in assigning constitutional formulæ to members of the terpene series. Recently, work on the absorption spectra and on the refractivity emphasises the great assistance which may be expected from these properties. A vivid controversy[17] between the supporters of the respective methods has served to show that the absorption spectra are more delicately sensitive to slight constitutional differences, for example, the degree of conjugation of a pair of double linkings,[18] but that the refractivity indicates with precision the different types of double linking. The purity of the terpene can be accurately gauged by means of the absorption spectra, very slight differences (0·1°) in the boiling point being reflected in the spectra. As an example of the results of the study of the absorption spectra of three isomeric *p*-menthadienes, limonene ($\Delta^{1:8}$) has less absorptive power than terpinolene ($\Delta^{1:4(8)}$) and terpinene. As the absorptive power of the two latter is nearly identical, it is proposed to revert to the former symbol ($\Delta^{1:4}$) for terpinene, notwithstanding the fact that the chemical evidence is decidedly in favour of the Harries' formula ($\Delta^{1:3}$). As the result of much laborious statistical work, data of refraction and dispersion have now been collected,[19] which render possible a sharp differentiation between endocyclic and semicyclic double linkings in hydroaromatic and similar compounds. Endocyclic unsaturated compounds are optically normal, whereas a semicyclic double linking causes an exaltation, both of the specific refraction and specific dispersion. In a number of pairs of isomeric hydrocarbons, which have been compared, alkylidene*cyclo*hexanes with alkyl-Δ^1-*cyclo*-

[17] K. Auwers, *Ber.*, 1911, **44**, 3525; 1912, **45**, 963; *A.*, ii, 4; ii, 505; A, Hantzsch, *Ber.*, 1912, **45**, 553, 559, 1742; *A.*, ii, 313, 709.

[18] C. R. Crymble, A. W. Stewart, R. Wright, W. G. Glendinning, and Miss F. W. Rea, *T.*, 1911, **99**, 451, 1262.

[19] K. Auwers and F. Eisenlohr, *Ann. Report*, 1910, 67; 1911, 51; K. Auwers and W. Moosbrugger, *Annalen*, 1912, **387**, 167; *A.*, ii, 213; K. Auwers and P. Ellinger, *ibid.*, 200; *A.*, i, 187; K. Auwers, *Ber.*, 1912, **45**, 2764, 2781; *A.*, i, 1013, 1015.

hexenes, the specific exaltation of the semicyclic compounds amounts to 0·28—0·47 of Σ_D, and to 6—10 per cent. of $\Sigma_\gamma - \Sigma_\alpha$. Δ^1-*cyclo*-Hexenylacetic acid and its derivatives are optically normal, whilst the isomeric *cyclo*hexylideneacetic acid and its derivatives show an even greater exaltation than the hydrocarbons—a behaviour which is attributed to the conjugated double linking present with the semicyclic linking. It is suggested that the constitution assigned to many hydrocarbons is in this respect erroneous; for example, many of Sabatier and Mailhe's alkylidene*cyclo*hexane derivatives are, in fact, endocyclic hexenes; and Zelinsky and Gutt's 3-methyl-1-ethylidene*cyclo*hexane must be 3-methyl-1-ethyl*cyclo*hexene.[20]

Among the numerous observations which have been recorded, the depression in refractivity which is not accompanied by a similar depression of the dispersing power, of unsaturated five-membered rings, containing the group ·CH:CH·CH:CH·, is shown to hold for homocyclic as well as heterocyclic compounds.[21] Previously the optical abnormality of *cyclo*pentadiene was thought to be due to its ready polymerisation, but the monomeric form, which is now found to be not difficult of preparation,[22] gives similarly low optical constants.

In a similar manner Östling[23] has made measurements and accumulated data of the refractive and dispersive powers of compounds possessing a *cyclo*propane or a *cyclo*butane ring; twenty-five of the former and sixteen of the latter class were available. The increment in the molecular refraction (M_α) due to the closing of the *cyclo*propane ring is +0·67, and to the closing of the *cyclo*butane ring +0·45. The molecular dispersion is unaffected. The conjugation of the *cyclo*propane ring with a double linking raises the value of the increment somewhat, but the effect of this conjugation is not perceptible when an alkyl or alkyloxy-group is attached to a central carbon atom of the system. Data are now available for making a preliminary comparison as to the relative sensitiveness of molecular refraction and magnetic rotation to constitutive influences:

	Change in molecular refraction.	Change in magnetic rotation.
Formation of 5- or 6-membered ring	−2·2	−0·6
,, ,, *cyclo*propane ring	−1·5	−0·5
,, ,, a double linking	−0·5	+0·7

cyclo*Octatetraene*.—The preparation of *cyclo*octatetraene, which is one of the most remarkable discoveries of the year, by Will-

[20] *Ber.*, 1902, **35**, 2142; *A.*, 1902, i, 585.
[21] K. Auwers, *ibid.*, 1912, **45**, 3077; *A.*, i, 956.
[22] H. Stobbe and F. Reuss, *Annalen*, 1912, **391**, 151; *A.*, i, 842.
[23] *T.*, 1912, **101**, 457.

stätter[24] and Waser from *N*-methylgranatenine, $C_8H_{11}\cdot NH\cdot CH_3$, obtained from the alkaloid ψ-pelletierine, was achieved by use of the very elegant method of eliminating two atoms of hydrogen first used in preparing *cyclo*heptadiene from suberone.[25]

From the quaternary methylammonium base from *N*-methylgranatenine, *cyclo*octatriene (I) was obtained by distillation in a high vacuum:

$$C_8H_{11}\cdot N(CH_3)_3\cdot OH = C_8H_{10} + N(CH_3)_3 + H_2O.$$

$$\begin{matrix}CH{:}CH{-}CH{:}CH\\ |\qquad\qquad |\\ CH_2\cdot CH_2\cdot CH{:}CH\end{matrix} \longrightarrow C_8H_{10}Br_2 \longrightarrow C_8H_{10}[N(CH_3)_2]_2 \longrightarrow$$

(I.)

$$C_8H_{10}[N(CH_3)_3\cdot OH]_2 \longrightarrow \begin{matrix}CH{:}CH\cdot CH{:}CH\\ |\qquad\qquad |\\ CH{:}CH\cdot CH{:}CH\end{matrix}.$$

The scheme shows the series of changes in which the tetraene is finally isolated.

In a similar manner[26] *cyclo*hexanol was converted into benzene. The $\Delta^{1:3}$-*cyclo*hexadiene,[27] which was passed en route, can be prepared in this way in a purer state than by treatment of *cyclo*hexene dibromide with quinoline:

$$C_6H_{11}\cdot OH \longrightarrow C_6H_{10} \longrightarrow C_6H_{10}Br_2 \longrightarrow C_6H_9\cdot NMe_2 \longrightarrow C_6H_8 \longrightarrow C_6H_8Br_2 \longrightarrow C_6H_8(NMe_2)_2 \longrightarrow C_6H_6.$$

The octatetraene at higher temperatures undergoes a rearrangement to an isomeride, which is unsaturated, but no longer has four double linkings, nor can be reduced to *cyclo*octane, but only to the compounds C_8H_{14} or C_8H_{12}. The most probable explanation of this change is that a more stable configuration has been produced with the formation of a di- or tri-cyclic compound:

$$\begin{matrix}CH\cdot CH\cdot CH{:}CH\\ ||\quad |\quad\quad |\\ CH\cdot CH\cdot CH{:}CH\end{matrix} \quad \text{or} \quad \begin{matrix}CH\cdot CH\cdot CH\cdot CH\\ ||\quad |\quad |\quad ||\\ CH\cdot CH\cdot CH\cdot CH\end{matrix}.$$

This fact has led to the suggestion that caoutchouc (dehydrocaouprene) has a similar cyclic structure[28]:

$$\begin{matrix}CH\cdot CH\cdot CH\cdots CH\\ ||\quad |\quad\quad ||\\ CH\cdot CH\cdot CH\cdots CH\end{matrix}.$$

Reducing Agents.—There has been much discussion during the period under review as to the efficacy and trustworthiness of the

[24] *Ber.*, 1911, **44**, 3423; *A.*, i, 17.

[25] *Ibid.*, 1901, **34**, 129; *A.*, 1901, i, 223.

[26] *Ibid.*, 1912, **44**, 1464; *A.*, i, 544.

[27] A. W. Crossley, *T.*, 1904, **85**, 1403; C. D. Harries, *Ber.*, 1912, **45**, 809, 2586; *A.*, i, 343, 842; N. D. Zelinsky and A. Gorsky, *Ber.*, 1911, **44**, 2312; *A.*, 1911, i, 847.

[28] I. von Ostromisslensky, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 204; *A.*, i, 280.

reducing agents which are in use for the addition of hydrogen to cyclic carbon compounds. Wallach[29] has pronounced in favour of Paal's reagent, that is, colloidal palladium (or platinum) and hydrogen,[30] as being less prone to cause constitutional change than any other. Willstätter,[31] on the other hand, presses the advantage of platinum-black and hydrogen preferably in the presence of acetic acid—a reagent to which attention has been drawn by Fokin.[32] It is claimed that this method is far superior to that of Sabatier and Senderens,[33] in that the hydrogenation is quantitative, and can be carried out at the ordinary temperature. There seems, however, to be as yet some difficulty in its application,[34] but this is ascribed to the presence of sulphur compounds (for example, thiophen), which inhibit the reduction of such compounds as benzene, naphthalene, benzoic acid, etc., but only retard the reduction of cyclic olefines, such as limonene. It is noteworthy that caoutchouc dissolved in benzene is not attacked by this reagent, but the solvent is reduced to hexane if the caoutchouc be not vulcanised.[35]

Numerous applications[36] of this method to the most diverse types of compounds are found in the literature of the year; and a critical investigation to determine the best procedure has been made by Skita.[37]

The synthesis of nitriles of this series by the interaction of magnesium alkyl bromides and cyanogen is also noteworthy; it offers a means of preparing saturated cyclic nitriles, acids, and so forth.[38]

During the period under review, continuous progress has been made with the syntheses of *o*-, *m*-, and *p*-menthenols, and the corresponding menthadienes.[39] An interesting method[40] of preparing benzo(pheno-)*cyclo*heptadienes is found in the condensation of 2 : 2′-dimethyldiphenyl-ωω′-dicarboxylonitrile under the influence of

[29] *Annalen*, 1911, **381**, 51; *A.*, 1911, i, 469.

[30] C. Paal, *A.*, 1905, ii, 397, 533; 1907, ii, 559; 1908, i, 599; 1909, i, 926; 1912, i, 703; A. Skita and H. Ritter, *Ber.*, 1910, **43**, 3393; *A.*, 1911, i, 71.

[31] *Ber.*, 1911, **44**, 3423; *ibid.*, 1912, **45**, 1164, 1471; *A.*, 1912, i, 17, 544, 545.

[32] *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276, 700; *A.*, 1908, i, 311; ii, 637.

[33] Compare G. B. Neave, *T.*, 1912, **101**, 513.

[34] H. Wieland, *Ber.*, 1912, **45**, 484, 2615; *A.*, i, 247, 956.

[35] F. W. Hinrichsen and R. Kempf, *ibid.*, 2106; *A.*, i, 687.

[36] L. C. Kelber and A. Schwarz, *ibid.*, 1946; *A.*, i, 617; A. Kötz and E. Schaeffer, *ibid.*, 1952; *A.*, i, 603.

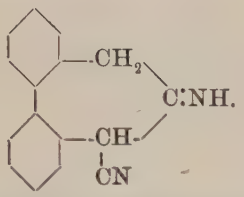
[37] *Ber.*, 1912, **45**, 3312, 3579, 3589; *A.*, 1913, i, 53, 54, 63.

[38] V. Grignard and E. Bellet, *Compt. rend.*, 1912, **155**, 44; *A.*, i, 623.

[39] W. H. Perkin, jun., and others, *T.*, 1911, **99**, 118, 518, 526, 727; G. G. Henderson and R. Boyd, *T.*, 1911, **99**, 2159.

[40] J. Kenner and Miss E. G. Turner, *ibid.*, 2101; *P.*, 1912, **28**, 277.

sodium ethoxide, when 1-imino-2-cyano-3 : 5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene was obtained:



What promises to be a very useful general method of converting ketones and aldehydes into hydrocarbons has been found [41] in the action of alcoholic sodium ethoxide on the semicarbazones or hydrazones:

$$>C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 \longrightarrow >C{:}N{\cdot}NH_2 \longrightarrow >CH_2 + N_2.$$

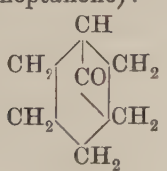
The temperature must be fairly high, 160—200°, but the amount of sodium ethoxide which apparently acts catalytically is of little importance. Fenchone and camphor are nearly quantitatively converted into fenchane and camphane respectively.

The problem of the conversion of unsaturated hydrocarbons to cyclic isomerides, the technical importance of which is of peculiar interest at the present time, was fully discussed in last year's report (pp. 107—108). The exact work on the polymerisation,[42] more especially of *as*-dimethylallene, $(CH_3)_2C{:}C{:}CH_2$, to *cyclo*butanes, has led to interesting results. Two types of dimerides are possible:

and ,

with three isomerides of each type. The three *cyclo*butanes of the first type have now been obtained by correct choice of conditions, and their constitutions settled by oxidation with ozone, but there is no sign of the dimerides of the second type.

The first example of the direct synthesis of a meta-linking in a six-membered ring is the formation of the norpinone [43] (bi*cyclo*-1 : 1 : 3-heptanone):



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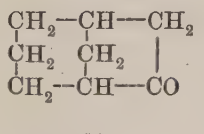

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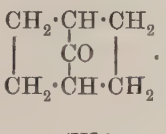


(III.)

[41] L. Wolff, *Annalen*, 1912, **394**, 86; *A.*, i, 988.

[42] S. V. Lebedeff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949; 1911, **43**, 820, 1735; *A.* 1911, i, 26, 774; 1912, i, 173; compare H. Stobbe and F. Reuss, *Annalen*, 1912, **391**, 151; *A.*, i, 842.

[43] O. Stark, *Ber.*, 1912, **45**, 2269; *A.*, i, 868.

The distillation of the calcium salt of homohexahydro*iso*phthalic acid results in the formation of a bi*cyclo*-1 : 2 : 2-heptan-3-one (II),[44] whilst similar treatment of the barium hexahydroterephthalate is said to yield the isomeric bi*cyclo*heptan-7-one (III).[45] Stark uses a similar method, namely, the distillation of calcium hexahydro*iso*phthalate. The reaction with bromine excludes the presence of a double linking, and hence of six- or seven-membered rings with a double linking as possible constitutions.

Ozonides and Oxozonides.—The abnormally large addition of oxygen which has frequently been observed in the combination of ozone with double linkings has now found an explanation in the discovery that ordinary strongly ozonised oxygen, "14 per cent. ozone," contains another polyatomic molecule, oxozone, probably O_4, besides ozone.[46] On washing crude ozone with sodium hydroxide and sulphuric acid, when the oxozone is destroyed, the abnormalities disappear and pure ozonides are obtained. An ozonide, RO_3, is not converted into an oxozonide, RO_4, by "mixed" ozone, hence pure oxozonides can only be prepared when their rate of formation is much speedier than that of the ozonides. So far this condition has only been found in the case of caoutchouc. The decomposition products of the oxozonide, $C_{10}H_{16}O_8$, are the same as those of the ozonide, but there is a greater proportion of lævulic acid than aldehyde.

Terpenes and Allied Compounds.—Of the very large number of papers, having as their subject the terpenes or ethereal oils, by far the greater proportion describe the extraction of these substances from various natural sources which have in recent years become more accessible. The methods of procedure appear to be becoming standardised; but the intricate chemistry of this vast group is not sufficiently explored to allow of the recognition of many of the compounds which have been isolated.

Camphene.—Since this puzzling member of the terpene series was last mentioned in the reports (1910), several investigators have been engaged with the attempt to solve the problem of its constitution. There seems now no doubt as to its individuality, and, moreover, that the materials obtained from all natural sources are identical.[47] Wagner's formula (I) has steadily risen in favour, replacing Semmler's (XIV), mainly owing to the simplicity of the oxidation of camphene by ozone[48]; dimethylnorcampholide and

[44] G. Komppa and T. Hirn, *Ber.*, 1903, **36**, 3610; *A.*, 1904, i, 60.

[45] N. D. Zelinsky, *ibid.*, 1901, **34**, 3800.

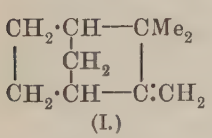
[46] C. D. Harries, *Zeitsch. Elektrochem.*, 1912, **18**, 130; *A.*, ii, 343; *Ber.*, 1912, **45**, 936; *A.*, i, 407; *Annalen*, 1912, **390**, 235; *A.*, i, 673.

[47] O. Aschan, *Annalen*, 1911, **383**, 1, 39; *A.*, 1911, i, 794, 796.

[48] F. W. Semmler, *Ber.*, 1909, **42**, 246, 962; *A.*, 1909, i, 170, 312; C. D. Harries and J. Palmèn, *Ber.*, 1910, **43**, 1432; *A.*, 1910, i, 497.

camphenilone, the products, are certainly represented by the formulæ (II) and (III), since the latter has been converted into the acid (IV), the constitution of which has been demonstrated by direct synthesis.[49] Among other difficulties in the way of accepting Wagner's formula is the fact that some 70 per cent. of the product of oxidation of camphene is camphenic ("camphenecamphoric") acid.[50] The constitution of this acid was given by Aschan, who proposes the formula (V) on the grounds that it only formed a monobromo-derivative, which could be converted through an unsaturated acid (VIII) to a hydroxy-acid (VII), which does not form a lactone. Moreover, the unsaturated acid yields the lactone of a tribasic acid (IX), the constitution of which was based on the results of alkali-fusion. W. N. Haworth and A. T. King [51] have, however, synthesised in a simple manner a lactone of this constitution, which differs unmistakably from Aschan's compound. Hence much of the evidence for the constitution ascribed to camphenic acid fails. Haworth and King suggest that since a second isomeride of the acid is known,[52] Aschan's acid may have the constitution (XI), when camphenic acid would have the formula (XII).

The formation from bornylene (XIII) of camphenilanaldehyde, which can be prepared simply by several different methods from camphene, as well as other considerations, has led G. G. Henderson and I. M. Heilbron [53] to urge that the carbon-skeleton of camphene and bornylene is more closely related than is shown by Wagner's and Aschan's (VI) formulæ, and to suggest the revival of Semmler's formula (XIV), as that which permits the formation of the aldehyde, with the least rearrangement from both hydrocarbons.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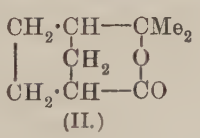
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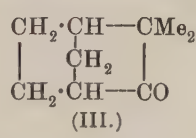
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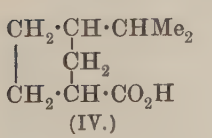
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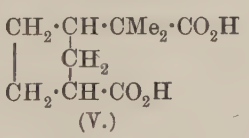
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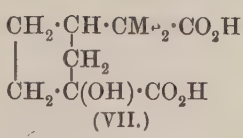
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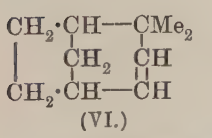
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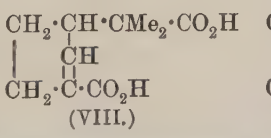
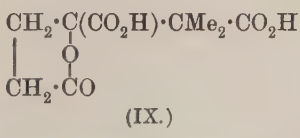
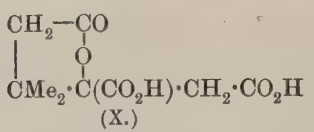
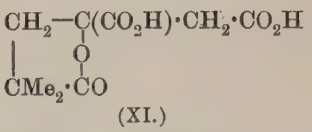

(VIII.)


(IX.)

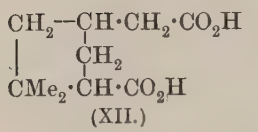
[49] L. Bouveault and G. L. Blanc, *Compt. rend.*, 1908, **147**, 1314; *A.*, 1909, i, 108.
[50] O. Aschan, *Annalen*, 1910, **375**, 336; *A.*, 1910, i, 709.
[51] *T.*, 1912, **101**, 1975.
[52] W. H. Perkin, jun., and J. F. Thorpe, *ibid.*, 1901, **79**, 764.
[53] *T.*, 1911, **99**, 1887, 1901.



(X.)



(XI.)



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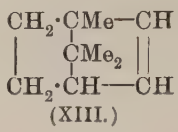
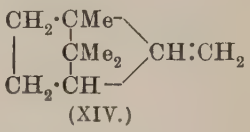
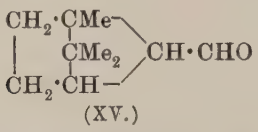


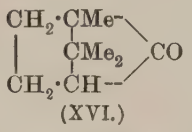
(XIII.)



(XIV.)



(XV.)



(XVI.)

This view necessitates an alteration of the formulæ of both camphenilanaldehyde and camphenilone [Henderson's and Heilbron's formulæ are respectively (XV) and (XVI)]. That of the last-named seems, however, fairly certain, and has found confirmation on further recent study.[54]

A very striking light is thrown on the constitution of camphene by its spectro-chemical properties.[55] It shows a molecular optical exaltation or increment (M_D) of $+2{\cdot}12$, which, as was stated in the foregoing, could not be caused by an endocyclic, but only a semicyclic ethylene linking. Moreover, the exaltation which has been shown to be caused by a tricyclic linking, whether in *cyclo*propane derivatives,[56] or in terpenes (cyclene, etc.), does not exceed $+0{\cdot}9$; hence camphene cannot be a saturated compound possessing such a structure. Finally, the normal refractivity of *iso*camphane[57] (dihydrocamphene) demonstrates that the increment cannot be attributed to the carbon-skeleton of camphane. Aschan's formula seems, therefore, to be excluded in favour of Wagner's, or possibly Semmler's, both of which have a semicyclic ethylene linking.

Camphor.—Among the numerous researches dealing with derivatives of camphor, some of which have rather a secondary objective, the investigation of the behaviour of the various groups, weighted by the camphor complex,[58] or a study of morphotropic relations,[59] attention may be directed to the reinvestigation, which

[54] S. V. Hintikka and G. Komppa, *Annalen*, 1912, **387**, 293; *A.*, i, 278.

[55] K. Auwers, *ibid.*, 240; *A.*, ii, 214.

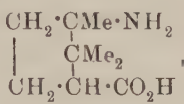
[56] G. J. Östling, *T.*, 1912, **101**, 457.

[57] P. Lipp, *Annalen*, 1911, **382**, 285; *A.*, 1911, i, 731.

[58] M. O. Forster and collaborators, *T.*, 1911, **99**, 478, 1982; 1912, **101**, 1327; A. Haller, *Compt. rend.*, 1912, **154**, 742; *A.*, i, 359; J. Bredt, *Ber.*, 1912, **45**, 1419; *A.*, i, 411; *J. pr. Chem.*, 1911, [ii], **84**, 786; *A.*, i, 112.

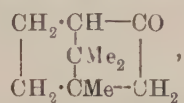
[59] W. H. Glover and T. M. Lowry, *T.*, 1912, **101**, 1902.

is accompanied by a re-naming, by Noyes and his pupils,[60] of the degradation products of camphor. It seems that in the formation of the *cis*- and *trans*-hydroxydihydrocampholytic acids from amino-dihydrocampholytic acid,



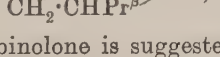
if the stereoisomerism of the hydroxy-acids is accepted, change of the type of the Walden inversion occurs. It is worthy of mention that the period under review has seen the close of a famous controversy concerning the synthesis of camphoric acid[61]; it is now admitted that Komppa's synthesis[62] is well founded.

Another isomeride of camphor, epicamphor, or β-camphor,



which has recently been prepared,[63] but by somewhat inconvenient processes, has now been obtained easily from methyl bornylenecarboxylate.[64] With hydroxylamine this compound yields the hydroxamic acid, $C_{10}H_{15}$·C(OH):NOH, which on heating decomposes into epicamphor and ammonia. Both the stereoisomerides of *iso*nitroso-epicamphor, together with other nearly-related compounds, have been prepared through phenyliminocamphor from camphorquinone, of which all the oximes are now known.[65]

iso*Camphor*.—A very interesting discovery has been made by Wallach[66] with regard to the constitution of this isomeride of camphor. Under conditions, the use of colloidal palladium, which admit of no profound change, it has been found that the reduction of *iso*camphor gives dihydropinolone, which is 1-acetyl-3-*iso*propyl-*cyclo*pentane. Hence *iso*camphor, which is not identical with pinolone, is a 1-acetyl-3-*iso*propyl*cyclo*pentene,



for which the name *iso*pinolone is suggested.

[60] *J. Amer. Chem. Soc.*, 1912, **34**, 62, 174, 1067; *A.*, i, 159, 786.

[61] G. L. Blanc and J. F. Thorpe, *T.*, 1910, **99**, 2010; G. Komppa, *ibid.*, 29.

[62] *Ann. Report*, 1904, 112.

[63] F. R. Lankshear and W. H. Perkin, jun., *P.*, 1911, **27**, 166; J. Bredt and W. Hilbing, *Chem. Zeit.*, 1911, **35**, 765; *A.*, 1911, i, 657.

[64] J. Bredt and W. H. Perkin, jun., *P.*, 1912, **28**, 56.

[65] M. O. Forster and H. Spinner, *T.*, 1912, **101**, 1340.

[66] *Annalen*, 1912, **392**, 49; *A.*, i, 879; compare *Annalen*, 1911, **384**, 193; *A.*, 1911, i, 891.

Natural Products.

Tannin.—With the synthesis[67] of compounds which closely resemble tannin a great advance has been made in the attempt to determine the chemical nature of this substance. Although it was originally supposed that tannin was a compound of sugar and gallic acid,[68] the view that the essential constituents of the material was a digallic acid has found general acceptance, and alone appears in the textbooks.[69] The low acidity, small electrical conductivity, and high molecular weight,[70] however, render this hypothesis untenable, and, moreover, have led Nierenstein[71] to abandon his view that tannin was a mixture of digallic and leucodigallic acids. His new formula represents tannin or tannins as polygalloylleucodigallic anhydrides[72]:

$$OH\cdot[C_6H_2(OH)_2\cdot CO\cdot O]_x\cdot C_6H_2(OH)<\begin{matrix}O\cdot CO\cdot C_6H_2(OH_2)\text{-}O\\ CO\cdot O\cdot C_6H_2(OH)_2\cdot CH\cdot OH\end{matrix}\cdot$$

the optical activity being due to the leucodigallic acid, and not to the presence of a glucose residue. Fischer and Freudenberg have satisfied themselves (*loc. cit.*) that purified tannin contains a small proportion (7—8 per cent.) of dextrose, which cannot be present as an impurity, and to which they ascribe the optical activity. The isolation of a crystalline glucogallic acid as a companion of tannin in certain galls as collateral evidence may be recorded.[73] They suggest that tannin is therefore a pentadigalloylglucose,[74] which should yield 10·6 per cent. of dextrose,

$$[C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2CO]_5C_6H_7O_6.$$

This compound is to be regarded rather as an ester than as a glucoside. Starting from trimethylcarbonatogalloyl chloride and dextrose, a pentagalloylglucose, $[C_6H_2(OH)_3\cdot CO]_5,C_6H_7O_6$, was prepared, which had the greatest resemblances to tannin, in taste, optical activity, slight acidity, colour reactions, and the power of forming precipitates with gelatin and alkaloids. Moreover, methyltannin, which is prepared from diazomethane and tannin, is identical with the material obtained from pentamethyldigalloyl chloride

[67] E. Fischer and K. Freudenberg, *Ber.*, 1912, **45**, 915, 2709 ; *A.*, i, 471, 887.

[68] A. Strecker, *Annalen*, 1852, **81**, 248 ; *ibid.*, 1854, **90**, 328.

[69] H. Schiff, *Ber.*, 1871, **4**, 232, 967 ; *ibid.*, 1879, **12**, 33.

[70] P. Walden, *ibid.*, 1897, **30**, 3151 ; 1898, **31**, 3167.

[71] *Ann. Report*, 1909, 107 ; *Ber.*, 1908, **41**, 77 ; 1909, **42**, 1122 ; 1910, **43**, 628 ; *A.*, 1908, i, 90 ; 1909, i, 897 ; 1910, i, 265 ; compare R. J. Manning and M. Nierenstein, *Ber.*, 1912, **45**, 1546 ; *A.*, i, 566.

[72] *Annalen*, 1912, **388**, 223 ; *A.*, i, 468.

[73] K. Feist, *Ber.*, 1912, **45**, 1493 ; *A.*, i, 566.

[74] Compare H. C. Biddle and W. P. Kelley, *J. Amer. Chem. Soc.*, 1912, **34**, 918 ; *A.*, i, 713.

and dextrose (Fischer and Freudenberg). Hence methyltannin,[75] which is a mixture probably of two stereoisomerides, is a penta-[pentamethyl]digalloylglucose. It is noteworthy that by this method compounds of very large molecular weight can be synthesised; thus there is no difficulty in preparing the compound from tribenzoylgalloyl chloride and glucose with a molecular weight of nearly 3000.[76]

Damascenine.—The synthesis[77] of damascenine, the "alkaloid" of *Nigella damascena*, has proved that Keller's[78] "betaine" formula is incorrect. Damascenine is methyl 2-methylamino-3-methoxybenzoate, which Keller isolated, but believed to be the methyl derivative of the alkaloid.

Scopoletin.—Another natural product, the constitution of which appears to be finally settled, is scopoletin; this compound is 2:4-dihydroxy-5-methoxyphenylpropionic acid, and can be converted with ease either into 2:4-dihydroxyanisole or 2:4-dihydroxy-5-methoxycinnamic acid.[79]

The most cursory perusal of the foregoing review in this section will show that much that is both important and interesting in the year's work is not even mentioned. In making a selection of the subjects to be reviewed, the extent to which they have been dealt with in the reports immediately preceding, has been taken into account; thus the organic compounds of arsenic and sulphur were fully considered last year, whereas little reference was made to the terpenes and hydroaromatic group. Moreover, it is obvious that a large proportion of the work in organic chemistry must be given simply to exploration; vast numbers of compounds which are possible on our present theories still remain to be prepared. The explorers mainly follow well-beaten tracts, and the new ground which is mapped out by a familiar procedure only occasionally shows features which differ more than in details from that already broken. That such work is absolutely necessary, and when considered as a whole forms a fine monument of achievement, is shown by several well known classic examples, but it does not lend itself to review at very frequent intervals.

KENNEDY J. P. ORTON.

[75] J. Herzig, *Ber.*, 1908, **41**, 2890; *A.*, 1908, i, 186; *Monatsh.*, 1909, **30**, 543; 1912, **33**, 843; *A.*, 1909, i, 713; 1912, i, 792.

[76] See also H. Crompton, *P.*, 1912, **28**, 193.

[77] A. J. Ewins, *T.*, 1912, **101**, 544.

[78] O. Keller, *Arch. Pharm.*, 1904, **242**, 299; 1908, **246**, 1; *A.*, 1904, i, 768; 1908, i, 283.

[79] C. W. Moore, *T.*, 1910, **97**, 2224; 1912, **101**, 1043.

Part III.—Heterocyclic Division and Stereochemistry.

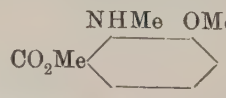
The notable features of the year's work appear to have been the advances which have been made in the study of alkaloids, and also the growing tendency to apply the conceptions of physical chemistry to the study of stereochemical problems. In the latter class mention may be made of the investigations of the Walden inversion mechanism, and also Michael's application of the entropy principle to stereoisomerides. These and kindred researches suggest that we may shortly see a considerable augmentation of interest in stereochemistry, and many of the problems which were left unsolved by the older methods may yield to the newer methods of attack.

The Alkaloids.

Summaries of alkaloid chemistry are exceptionally difficult to produce in any circumstances, owing to the intricate nature of the subject; and in the current year the task has been rendered even less easy than usual, for the progress during the last twelve months has been very marked, and consequently an enormous amount of material has accumulated which is very hard to weld into a connected whole without expending too much space. A selection of typical advances has, therefore, been made, preference being given to those points which lend themselves best to concise treatment. At the same time, it is hoped that a fair conspectus of the field as a whole has been furnished.

In view of the controversies which have arisen from time to time with regard to the natural syntheses of alkaloids which go on in plants, it is not without interest to find that Paternò and Maselli,[1] in the course of their studies in photochemistry, have discovered that when acetophenone is dissolved in a concentrated alcoholic solution of ammonia and then exposed to sunlight for several months, a 20 per cent. yield is obtained of a substance which appears to resemble the natural alkaloids in many respects. This product has the composition $C_{18}H_{18}N_2$, gives rise to various salts, and forms a nitroso-derivative. Up to the present, its constitution has not been determined.

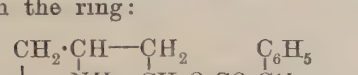
The simplest alkaloid synthesised during the year appears to be damascenine,[2] which has the structure:



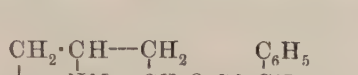
[1] *Gazzetta*, 1912, **42**, i, 65; *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 235; *A.*, i, 295.
[2] Ewins, *T.*, 1912, **101**, 544.

Strictly speaking, this compound does not fall into the present division of the subject, but it has been included on account of its simple structure and for the sake of completeness.

In the tropine group,[3] a substance hitherto termed ψ-hyoscyamine, and regarded as an isomeride of hyoscyamine, has recently been proved to be really nor-hyoscyamine, differing from hyoscyamine in having no methyl group attached to the bridge nitrogen atom in the ring:



Nor-hyoscyamine.



Hyoscyamine.

This relationship has been established by the following treatment. It was shown that the alkaloid contained no *N*-methyl group, whilst it formed a nitroso-compound, thus proving that it was a secondary amine. The action of methyl iodide on it produced a methyl derivative, which was found to be identical with *l*-hyoscyamine. Hydrolysis with barium hydroxide yielded tropic acid and nor-tropanol. Just as hyoscyamine is racemised and forms atropine, so nor-hyoscyamine can be converted into the optically inactive nor-atropine. In physiological properties there is a considerable difference between hyoscyamine and nor-hyoscyamine, the new alkaloid being eight times less active than the former in mydriatic action.

In the group of the cinchona alkaloids, various workers have studied the intramolecular changes which these substances can be made to undergo. Böttcher and Horovitz[4] find that when quinine is heated at 100° with sulphuric acid, two bases result, which they term A and B; and these compounds are also formed when quinine is treated with hydrogen iodide. It appears that the base B is identical with Lippmann and Fleissner's *iso*quinine.[5] A somewhat similar treatment seems to convert quinine and cinchonine into their poisonous isomerides, quinotoxine and cinchotoxine; for when a salt of quinine is heated at 95—98° in aqueous solution, with or without excess of acid, it undergoes rearrangement with the production of quinotoxine.[6] Cinchonine gives the analogous cinchotoxine. The velocity of the rearrangement appears to depend to a great extent on the strength of the acid employed; weak acids seem to favour the process, whilst strong acids, such as hydro-

[3] Carr and Reynolds, *T.*, 1912, **101**, 946.

[4] *Monatsh.*, 1911, **32**, 793; 1912, **33**, 567; *A.*, 1911, i, 1011; 1912, i, 717.

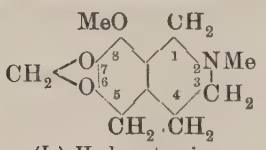
[5] *Ibid.*, 1891, **12**, 327; *A.*, 1892, 81.

[6] Biddle, *Ber.*, 1912, **45**, 526; *A.*, i, 296; Rabe, *ibid.*, 1447, 2927; *A.*, i, 488, 1014.

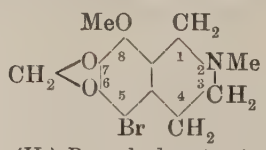
chloric, inhibit it. Even at a temperature of 36° the change takes place, although more slowly; and the same may be said for the exposure of salt solutions to direct sunlight at the ordinary temperature. Similar results were obtained with other members of the cinchona group.

Mention may be made of some preliminary synthetic experiments[7] in the cinchonine group, but the results could be satisfactorily dealt with only by entering into greater detail than space permits.

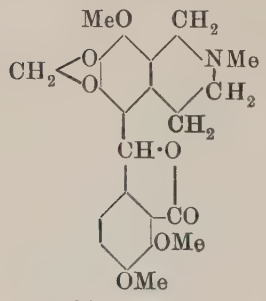
The group containing narcotine and its allies has been the centre of a considerable amount of investigation during the year. It will be remembered that Liebermann[8] endeavoured to produce narcotine by condensing together hydrocotarnine and opianic acid; but that, instead of the expected product, he obtained a substance, *iso*narcotine. The constitution of this substance has now been explained.[9] When hydrocotarnine (I) is treated with formaldehyde, the hydrogen atom left unsubstituted in the benzene ring (5) is attacked[10]; and this suggested that in the condensation which leads to *iso*narcotine the same hydrogen atom might be the one which becomes replaced by the opianyl radicle. To prove this, hydrocotarnine was brominated, thus exchanging the labile hydrogen atom for a bromine atom and producing bromohydrocotarnine (II). An attempt was made to condense the latter compound with opianic acid, but no reaction took place. This proves



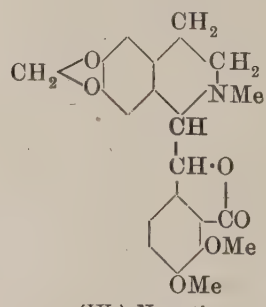
(I.) Hydrocotarnine.



(II.) Bromohydrocotarnine.



(III.) *iso*Narcotine.



(IV.) Narcotine.

[7] Rabe, *Ber.*, 1912, **45**, 2163; *A.*, i, 718.
[8] *Ber.*, 1896, **29**, 184, 2040; *A.*, 1896, i, 264.
[9] Freund and Fleischer, *ibid.*, 1912, **45**, 1171; *A.*, i, 490.
[10] Freund and Daube, *ibid.*, 1183; *A.*, i, 491.

that some factor is missing in the bromohydrocotarnine which is present in hydrocotarnine itself; and the missing factor can only be the labile hydrogen atom which is present in hydrocotarnine. The constitution of *iso*narcotine may therefore be written as shown on p. 156 (III), and the formula for narcotine is given in (IV) for comparison.

In connexion with the *iso*narcotine condensation, another point might be mentioned. Liebermann employed 73 per cent. sulphuric acid as his condensing agent; but later work by Kersten[11] showed that concentrated hydrochloric acid might also be used with good effect. The use of this reagent in the condensation of phenolic ethers appeared to Jones, Perkin, and Robinson[12] to leave some doubt as to the identity of products obtained in this way; and they have therefore investigated the behaviour of various ethers when submitted to condensation by this method. The results show that the reaction takes the ordinary course, so that a possible objection to the *iso*narcotine structure was thus removed.

The behaviour of narcotine when submitted to the action of heat in various solvents[13] has shown that decomposition ensues in alcoholic, aqueous, or acetic acid solution, whereas mineral acids have but little influence.

The condensation of cotarnine with nitromeconine produced a substance, nitrognoscopine.[14] This work has now been continued,[15] and it is found that when the nitro-compound is reduced to an amino-derivative, the latter yields a hydrazine, which, on oxidation, is converted into an isomeride of gnoscopine. It is suggested that *r*-narcotine should be termed α-gnoscopine, whilst the new stereoisomeride should be called β-gnoscopine; and there is reason to believe that the α-modification corresponds with racemic acid, and the β-form with *i*-tartaric acid. Similar reactions[16] have been applied to the preparation of anhydrohydrastininemeconine with very good results. Gnoscopine[17] appears to be produced when narcotine is heated in various solvents for long periods.

If a Grignard reagent prepared from ethylene bromide and magnesium is allowed to act on hydrastinine,[18] two isomeric dihydrohydrastinines are produced, which owe their isomerism to spatial differences. This reaction is similar to that discovered[19] in the

[11] *Ber.*, 1898, **31**, 2099; *A.*, 1898, i, 702.
[12] *T.*, 1912, **101**, 257.
[13] Rabe, *Ber.*, 1912, **45**, 2927; *A.*, i, 1014.
[14] Hope and Robinson, *P.*, 1910, **26**, 228.
[15] *Ibid.*, 1912, **28**, 16.
[16] *Ibid.*, 17.
[17] Rabe, *Ber.*, 1912, **45**, 2927; *A.*, i, 1014.
[18] Freund and Shibata, *ibid.*, 855; *A.*, i, 488.
[19] Freund and Kupfer, *Annalen*, 1911, **384**, 1; *A.*, 1911, i, 911.

case of cotarnine. The case is somewhat complicated by the presence of a methyl group attached to a nitrogen atom in the ring; and there is a possibility of *cis-trans*-isomerism entering into the question. If we assume such isomerism, two isomeric *meso*-forms of the substance would be possible.

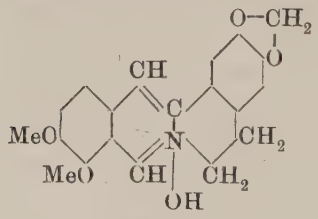
A general method whereby hydrastinine bases may be obtained from berberine derivatives has been devised,[20] the outline of which is as follows. The dihydroberberine derivative (I), in which R represents an alkyl, alkaryl, or aryl radicle in the α-position, is converted into the tetrahydro-compound (II), then into the quaternary compound (III), and finally into the ammonium base (IV) and the ψ-base. Further elimination of water may then take place, or oxidation will convert the base into derivatives of hydrastinine (V):

$$\underset{\text{(I.)}}{C_{20}H_{18}RO_4N} + H_2 = \underset{\text{(II.)}}{C_{20}H_{20}RO_4N}$$

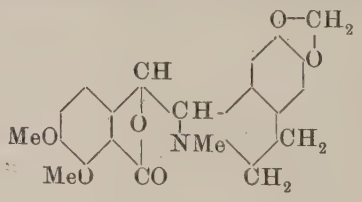
$$C_{20}H_{20}RO_4N + MeI = \underset{\text{(III.)}}{C_{20}H_{20}RO_4NMeI}$$

$$\underset{\text{(IV.)}}{C_{20}H_{20}RO_4NMeOH} = H_2O + \underset{\text{(V.)}}{C_{20}H_{19}RO_4NMe}$$

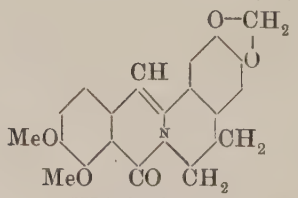
Turning now to the berberine group, a comparison of the formulæ of berberine (I) and hydrastine (II) will show that a



(I.) Berberine.



(II.) Hydrastine.



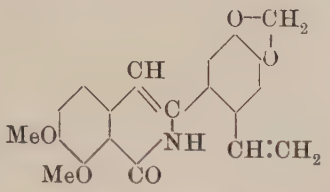
(III.) Oxyberberine.

close relationship exists between the two. Hydrastine is evidently the lactone corresponding with the unsaturated acid which would be obtained if a methyl group could be attached to the nitrogen atom of oxyberberine (III). With a view to producing this change,[21] oxyberberine was submitted to the action of methyl iodide

[20] Freund, D.R.-P. 241136; *A.*, i, 383.

[21] Bland, Perkin, and Robinson, *T.*, 1912, **101**, 262.

in the presence of water, but the ultimate product appears to be an isomeride of oxyberberine, which probably has the structure represented by:

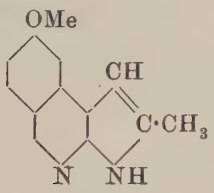


*iso*Oxyberberine.

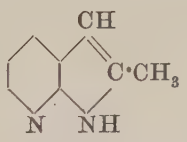
The function of the methyl iodide is apparently merely to furnish hydriodic acid, the presence of which is necessary to the reaction, for the conversion of oxyberberine into *iso*oxyberberine can equally well be produced by heating oxyberberine with hydrochloric acid.

Other work in the berberine series includes the preparation of numerous derivatives of berberine and tetrahydroberberine.[22]

A considerable amount of attention has recently been paid to the harmine group of alkaloids. Perkin and Robinson[23] consider that the following formula, since it affords an explanation of the reactions of harmine, must be very close to the actual constitution of the substance:



Harmine.



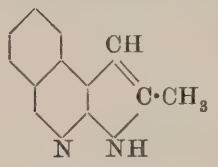
*apo*Harmine.

If this view be correct, then *apo*harmine should have the second formula above, which is 2-methylindole in which one of the methine groups of the benzene ring is replaced by a nitrogen atom. Such compounds containing a fused pyridine-pyrrole nucleus are unknown; and as each ring might be expected to modify the other's properties to some extent, the further experiments in the syntheses of such substances will be awaited with interest.

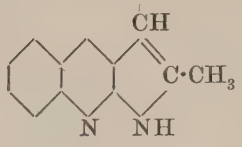
Now when the methoxy-group is eliminated from harmine,[24] a base, harman, is obtained, which, on the Perkin-Robinson view, would have either of the structures (I) and (II), according as harmine contains a quinoline or an *iso*quinoline nucleus. To throw

[22] Freund, D.R.-P. 242217; *A.*, i, 487.
[23] *T.*, 1912, **101**, 1775.
[24] O. Fischer, *Chem. Centr.*, 1901, i, 957; *A.*, 1901, i, 405.

some light on this, the latter substance has been synthesised,[25] and it is found not to be identical with harman, although very similar to it. The new substance (II) has therefore been termed *iso*harman.



(I.)



(II.)

From these results, it may be concluded that harmine itself contains an *iso*quinoline nucleus as shown above, and not one containing a quinoline group.

It has been shown[26] that, by heating harmic acid to 250—280° in a vacuum there is obtained from it *apo*harminecarboxylic acid, which in turn at 330° decomposes with loss of carbon dioxide, yielding *apo*harmine. From these results it is deduced that harmic acid is *apo*harmine-2 : 3-dicarboxylic acid. A new base[27] has been prepared from *apo*harmine by applying Hofmann's reaction. The decomposition does not take the usual course, but results in the formation of a substance containing four atoms of nitrogen, which appears to be trimethyldi*apo*harmine. It has also been shown that *apo*harmine can be reduced to a tetrahydro-derivative in addition to the dihydro-compound already known.[28]

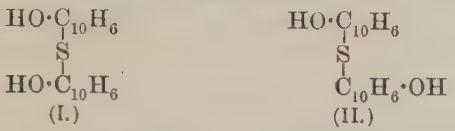
Some harmaline derivatives have been synthesised by O. Fischer and Boesler.[29]

β-Naphthasulphonium-quinone and the Sulphides of β-Naphthol.

When the α-sulphide of β-naphthol, $HO{\cdot}C_{10}H_6{\cdot}S{\cdot}C_{10}H_6{\cdot}OH$, is treated with alkaline oxidising agents, it loses two atoms of hydrogen, and is converted into a stable scarlet substance, first termed dehydro-β-naphthol sulphide. Reduction of this leads to the production of a naphthol sulphide, which appears to be different from the original one. This series of compounds was very thoroughly examined by Henriques,[30] who was unable to put forward any structural formulæ to explain the existence of the two isomerides, and therefore assumed that they were stereoisomeric, the sulphur atom being supposed in some way to hinder free

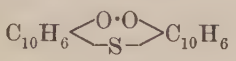
[25] Perkin and Robinson, *P.*, 1912, **28**, 154.
[26] Hasenfratz, *Compt. rend.*, 1912, **154**, 704 ; *A.*, i, 383.
[27] *Ibid.*, 1520 ; *A.*, i, 577.
[28] *Ibid.*, 1912, **155**, 284; *A.*, i, 797.
[29] *Ber.*, 1912, **45**, 1930 ; *A.*, i, 645.
[30] *Ibid.*, 1894, **27**, 2999 ; *A.*, 1895, i, 103.

rotation of the two naphthol groups, so that the spatial formulæ of the isomerides might be written as follows:



(I.) (II.)

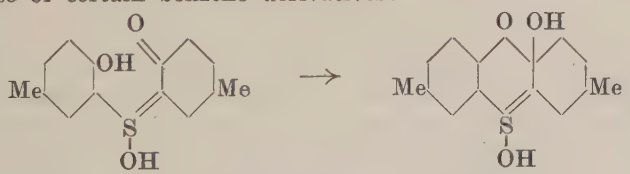
Thus, in the one case, the hydroxyl groups were on the same side of the molecule, whilst in the second isomeride they were on opposite sides. With regard to the structure of the intermediate scarlet substance, Henriques concluded that it was a peroxide of the formula:



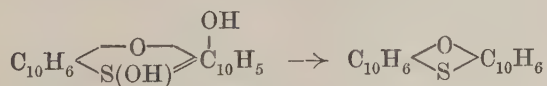
(III.)

This structure would agree with the known reactions of the substance up to a certain point, and is especially suitable in connexion with the hypothesis that the two sulphides are stereoisomeric, since in the reduction of the peroxide it is to be expected that a naphthol derivative of formula (I) (where the two hydroxyl groups are adjacent in space) would be formed in preference to one having the second formula.

The investigation of this series of substances has been undertaken by Smiles and his collaborators; and their investigation has led to wholly unexpected results. In the first place, the so-called peroxide reacts with phenylhydrazine, forming a dihydrazone, as Henriques had shown; and this in itself tends to throw some doubt on the applicability of the peroxide formula; for one would expect a true peroxide to be readily reduced by phenylhydrazine, giving the sulphide instead of the hydrazone. Secondly, the scarlet substance, when treated with alcoholic alkali hydroxide, produces a naphthathioxin. Now this result is parallel to those obtained [31] in the case of certain benzene derivatives:



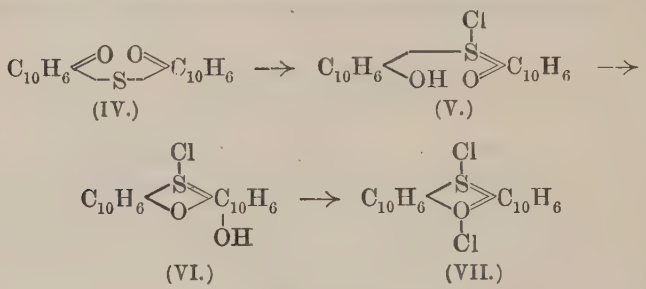
(IV.)



[31] Hilditch and Smiles, *T.*, 1911, **99**, 973.

so that it seems probable that the scarlet substance has the structure (IV), and is really β-naphthasulphonium-quinone. An examination of the new formula proposed for this substance shows that it contains a quinonoid nucleus of a totally new type, and its reactions are therefore of more than usual interest.

When treated with hydrogen chloride,[32] the quinone is converted into chloronaphthathioxin; whilst acetic anhydride in the presence of camphorsulphonic acid gives acetoxynaphthathioxin. Taking the case of the halogen acids, the reaction is formulated as follows:



(IV.) (V.)

(VI.) (VII.)

In the first place, the halogen acid attacks the quinonoid nucleus, but in so doing it produces a substance unstable in the presence of acids. This unstable substance tends to pass into a cyclic compound by intramolecular change; and an examination of this intermediate compound (VI) will show that it is a ψ-base, which hydrogen chloride would convert into the thioxonium salt (VII).

In the presence of an alcoholic solution of sodium ethoxide, the scarlet quinone is reduced to β-naphthol sulphide (m. p. 212°), namely, that from which the quinone was prepared. Now, Henriques, employing acid reducing agents, showed that an isomeric sulphide was formed (m. p. 153°); and the possibility of a ψ-base being formed as an intermediate product in this reaction furnishes a clue to the cause of the different results obtained in the two cases.

Turning now to the properties of the two sulphides themselves, it must be admitted that their isomerism must be of a peculiar character. If the hypothesis of stereoisomerism be accepted, a postulate is made which has no parallel in stereochemistry; so that it is clear that all other possibilities should be exhausted before falling back on this. An investigation of the actions of various reagents, such as sulphuric acid, potassium hydroxide, and ferric chloride, on the two isomerides has been made,[33] and it was

[32] Christopher and Smiles, *T.*, 1912, **101**, 710.

[33] Crymble, Ross, and Smiles, *ibid.*, 1146.

found that there are very marked differences between the two forms. Thus, cold sulphuric acid with the stable sulphide produces naphthathioxin oxide; whilst the unstable isomeride yields naphthathiophen. A more striking difference even than this is observed when bromine is allowed to act on the two sulphides.[34] The stable compound yields bromo-derivatives of β-naphthol, the sulphur being eliminated in exchange for the halogen; the unstable sulphide, on the other hand, retains the sulphur atom and takes up three atoms of bromine in exchange for hydrogen. The tribromo-derivative formed in this last reaction readily gives up hydrogen bromide on treatment with pyridine, yielding a stable crimson substance, which appears to be dibromonaphthasulphonium-quinone.

The absorption spectra[35] of the two sulphides appear to resemble each other to some extent in general character. Each contains two bands, which have their heads at 3000 and 3500 units respectively.

Residual Affinity and Spatial Conjugation.

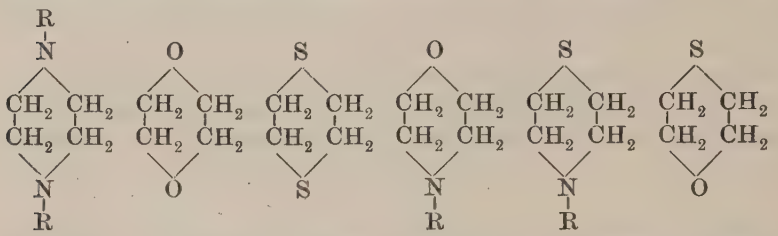
It is a well-known fact that when two unsaturated groups in a molecule are conjugated structurally, their mutual influence to some extent destroys the specific character of each; for instance, the double bonds in the structure ·CH:CH·CH:CH· do not behave like ordinary isolated double bonds. Now it is known that in a normal carbon chain the positions 1:5 and 1:6 have certain properties which lead to the assumption that they are closely situated with regard to each other in space; and the same has been noticed with regard to the 1:4-positions in a six-membered cyclic substance. We are thus driven to inquire whether any mutual influence can be traced between two unsaturated groups which, although structurally unconnected, are placed in close proximity to one another in space.

An examination[36] of optically active esters and salts of saturated aliphatic acids which had two carboxyl radicles at the ends of a normal chain of carbon atoms has been made; and it was found that anomalous rotatory powers were shown when the carboxyl groups were in the 1:5- and 1:6-positions with regard to each other. This is an example of what is termed "spatial conjugation."

A very complete investigation of space-conjugation of the second type, in which the unsaturated groups lie in the 1:4-position with

[34] Nolan and Smiles, *T.*, 1912, **101**, 1420; Ross and Smiles, 1912, **28**, 275.
[35] Crymble, Ross, and Smiles, *ibid.*, 1146.
[36] Hilditch, *ibid.*, 1909, **95**, 1578.

regard to one another in a saturated ring, has led to interesting results.[37] The substances examined were the following:



Piperazines. 1 : 4-Dioxan. 1 : 4-Dithian. Morpholines. 1 : 4-Thiazans. 1 : 4-Thioxan.

and it will be observed that this series covers all possible permutations and combinations of the three atoms: nitrogen, sulphur, and oxygen.

Measurements of the reactivity of the various non-carbon atoms were made both qualitatively and quantitatively. In the latter case the method employed consisted in the addition of an alkyl bromide to the complex, by which means an "onium" salt was formed; and the amount of bromine thus converted into the ionisable condition was estimated by titration at fixed intervals. In each series the corresponding methylene compound was used as a standard; thus, piperidine derivatives were compared with the corresponding morpholine and thiazan compounds. It was assumed that deviations from the normal standard were due to the mutual influence of the two non-carbon atoms in the 1 : 4-position with regard to each other.

The chief results obtained may be summarised as follows: In cyclic compounds of the type:

$$X<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>Y,$$

in which X and Y are atoms capable of raising their valency (for example, nitrogen rising from triad to pentad), and may therefore be supposed to have some residual affinity unsatisfied, the two atoms X and Y do actually influence each other's reactivities. Further, if X and Y be atoms of the same element, their reactive power is increased; whereas if X and Y are atoms of different elements (as in the morpholines) their reactivity is diminished by the spatial conjugation. The physical constants of the various substances mentioned above have been examined, but in this direction the results have not been striking.

These results are of considerable importance, as they establish beyond question that two non-adjacent centres (structurally speaking) can influence each other's chemical reactive power to a marked

[37] Clarke, *T.*, 1912, **101**, 1788.

degree; and it may be anticipated that the observation that similar atoms stimulate one another whilst different elements diminish each other's reactivity will prove of value in further research along the same lines, and may even provide a better knowledge of the behaviour of such atoms when structurally conjugated.

The same branch of the subject has been attacked from a different point of view.[38] It has been shown that if the absorption spectra of various stereoisomerides are examined, the two structurally identical compounds do not always exhibit identical spectra. In those cases in which the two isomerides differ markedly from each other in spectra, it was found that the change from one isomeride to the other entailed the shifting in space with regard to one another of two centres of residual affinity; and that when the compounds did not fulfil this condition the difference in their spectra was very slight, or even in some cases non-existent. It would therefore seem of interest if the cyclic compounds formulated above were investigated spectroscopically, as it appears probable that the results might be important.

The Chlorophyll Question.

This subject hardly lends itself to annual summarisation, and in future it would be preferable to devote a section to it at such times as would enable the reporter to give a connected account of several years' work, so that the reader need not be confused with details carried on from year to year. In the present section no attempt could be made to cover the whole field of work; all that was possible was to take up one or two points which appear likely to have a bearing on future investigations.

It may be recalled that if chlorophyll (phytyl chlorophyllide) is treated with acids, it is decomposed into phæophytin (phytyl phæophorbide); and that this substance when subjected to alkalis produces a mixture of phytochlorine-*e* and phytorhodin-*g*. The fact that the two latter substances are always produced in practically constant quantities (1 mol. of the former to 2·5 mols. of the latter) whilst their molecular weights (after allowing for loss of phytol and methyl alcohol) approximate to that of chlorophyll, has suggested that chlorophyll may be a mixture of two substances, one of which on degradation yields phytochlorine-*e*, whilst the other is a phytorhodin-*g* derivative. This view has now been shown to be correct[39] by the separation of chlorophyll itself into two compounds, one of which, chlorophyll-*a*, is bluish-green, and yields only phytochlorine-*a* as a degradation product, whilst the other, chlorophyll-*b*, is

[38] Macbeth, Stewart, and Wright, *T.*, 1912, **101**, 599.

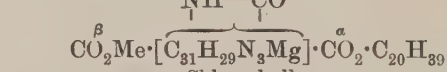
[39] Willstätter and Isler, *Annalen*, 1912, **390**, 269; *A.*, i, 710.

yellowish-green in colour, and produces only phytorhodin-*g* when it is decomposed. The intermediate decomposition product of chlorophyll, phæophytin, has also been shown to be a mixture of two substances.

The same process was applied at a slightly earlier date [40] to some chlorophyll derivatives. Chlorophyll, as is known, is phytyl chlorophyllide; and since the chief problem at issue is the constitution of the non-phytyl portion of the molecule, it seemed simpler to replace the phytyl group by ordinary alkyl radicles. In this way methylchlorophyllide and its homologues are produced. These substances have now been shown to be mixtures of the *a* and *b* chlorophyllides, which give rise to the corresponding phæophorbides *a* and *b*.

It will be remembered that in alcoholic solution chlorophyllides and alkylchlorophyllides undergo certain changes which produce substances different from the original one employed.[41] The term "allomerism" is now applied to such processes, and it is suggested that they are probably due to a rupture of the lactam group in the chlorophyll derivative and the subsequent formation of a new lactam form. It has been shown that allomeric change can be catalytically accelerated by the presence of glass; it is prevented by the addition of a trace of acid, and is unaffected by either platinum or silver.

The results of various methods of decomposing chlorophyll can be followed on the formula below:



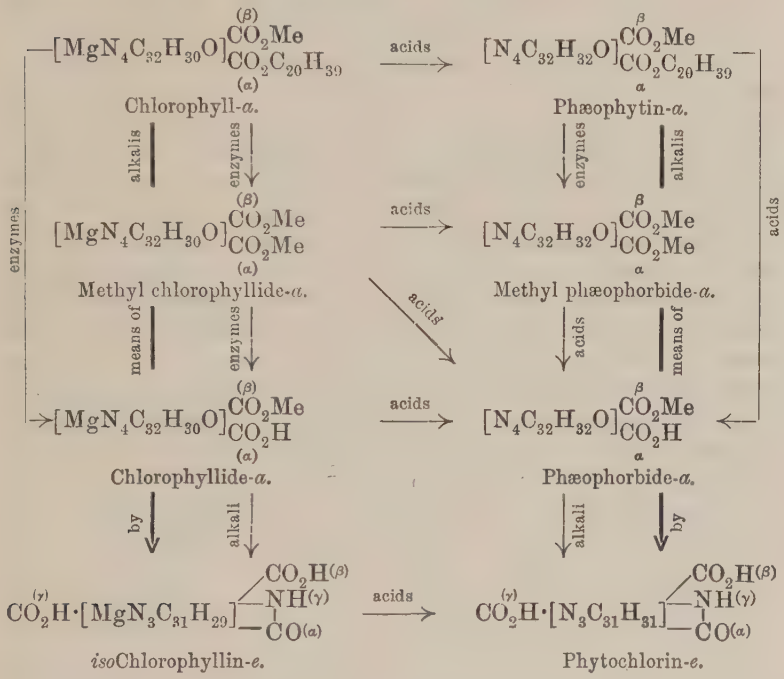
Chlorophyll-*a*.

(*A*) If chlorophyll is submitted to the action of the enzyme chlorophyllase, the α-group alone is attacked. The resulting substances depend on the solvent used: in methyl or ethyl alcohol the methyl or ethyl group replaces the phytyl nucleus, whilst in aqueous acetone solution the phytyl radicle is replaced by a hydrogen atom, yielding the free chlorophyllide. (*B*) If chlorophyll is acted on by acids there occurs, as a result of gentle treatment, a displacement of magnesium by hydrogen; and the corresponding phæophytin is liberated. More vigorous treatment results in hydrolysis at the α-group, with the formation of free phæophorbides. No allomerism occurs under this treatment, showing that the original lactam group is unaffected. (*C*) The first point of attack of alkalis is the γ-lactam group, a new lactam group being subsequently produced. The next action is hydrolysis at the α-group. Finally, with more

[40] Willstätter and Stoll, *Annalen*, 1912, **387**, 317; *A.*, i, 285.

[41] Willstätter and Utzinger, *ibid.*, 1911, **382**, 129; *A.*, 1911, i, 659.

difficulty, the β-group undergoes hydrolysis. At higher temperatures alkalis cause the elimination of carbon dioxide, resulting in a degradation to phyllins and porphorins. The following diagrammatic scheme will make the results clear:



Several investigations of the absorption spectra of chlorophyll derivatives have been made during the past year,[42] and the case is rather an exceptional one, since it has been found that in this series chemical methods are more delicate than spectroscopic ones. This is probably due to the great complexity of the chlorophyll nucleus, and also to the fact that the absorption spectra were not extended far into the ultra-violet in this particular case.

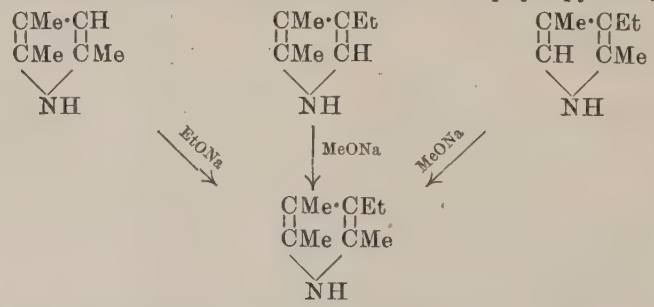
A considerable amount of work has been carried out on the porphorin group,[43] but it does not lend itself to detailed treatment in this place.

[42] Willstätter, Stoll, and Utzinger, *Annalen*, 1911, **385**, 156; *A.*, i, 40; Dhéré and Rogowski, *Compt. rend.*, 1912, **155**, 653; *A.*, i, 887; Marchlewski, *Biochem. Zeitsch.*, 1912, **43**, 234; *A.*, i, 791.

[43] Marchlewski and Robel, *Ber.*, 1912, **45**, 816; *A.*, i, 376; *Biochem. Zeitsch.*, 1912, **39**, 6; *A.*, i, 290; Marchlewski and Zurkowski, *Biochem. Zeitsch.*, 1912, **39**, 59; *A.*, i, 290; Marchlewski, *Annalen*, 1912, **388**, 63; *A.*, i., 288; Malarski and Marchlewski, *Biochem. Zeitsch.*, 1912, **42**, 219; *A.*, i, 641.

Phyllopyrrole and Haemopyrrole.

When hæmine is reduced with hydrogen iodide and phosphonium iodide it yields among other products the substance hæmopyrrole, which can also be produced as a decomposition product of chlorophyll. With a view to comparing the pyrrole derivatives which form part of the nuclei of chlorophyll and hæmine, both compounds were subjected to degradation processes,[44] and it was found that the final hæmopyrrole produced was not a single substance, but was a mixture of three pyrrole derivatives, which were named respectively, phyllopyrrole, hæmopyrrole,[45] and *iso*hæmopyrrole.[45] The conclusive proof of the constitution of these compounds by synthesis was not at that time forthcoming; but in the present year their structures have been placed beyond doubt. It has been shown that when sodium methoxide or ethoxide is allowed to act on pyrrole derivatives at high temperatures in alcoholic solution, the result is a displacement of the hydrogen atoms of the methine groups by methyl or ethyl radicles. By applying this process to certain trisubstituted pyrrole compounds, the synthesis of phyllopyrrole has been accomplished.[46] The scheme below shows that the results leave no doubt as to the constitution of phyllopyrrole;



The constitution of hæmopyrrole (Willstätter and Asahina's *iso*-hæmopyrrole) has been definitely settled by a process of exclusion.[47] Hæmopyrrole is a trisubstituted pyrrole, which can be converted into methylethylmaleimide; this proves that the ethyl group is in the β-position in the pyrrole ring. Further, when hæmopyrrole is ethylated, it yields a substance which is not identical with 2:4-dimethyl-3:5-diethylpyrrole; therefore this compound obtained from

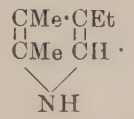
[44] Willstätter and Asahina, *Annalen*, 1911, **385**, 183; *A.*, i, 41; H. Fischer and Bartholomäus, *Ber.*, 1911, **44**, 3313; *A.*, i, 50.

[45] Fischer and Bartholomäus, (*Ber.*, 1912, **45**, 1979; *A.*, i, 646) propose to invert these names, since Willstätter's *iso*-compound forms the major part of the mixture.

[46] Fischer and Bartholomäus, *Ber.*, 1912, **45**, 466; *A.*, i, 297; compare Colacicchi, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 489; *A.*, i, 646.

[47] *Ibid.*, 1979; *A.*, i., 646.

hæmopyrrole must have the two ethyl groups on the same side of the molecule. Hence the hydrogen atom replaced in this ethylation process must lie in the α-position next the ethyl radicle, which furnishes the following constitution for hæmopyrrole:



This evidence is supported by the fact that a synthesis of 2:3-dimethyl-5-ethylpyrrole showed that this substance was different from hæmopyrrole.

A third pyrrole derivative, 2:4-dimethyl-3-ethylpyrrole, has been isolated from the hæmopyrrole mixture, and to this the name cryptopyrrole has been given. Its constitution has been established by a comparison with the synthetic substance. The proportions in which these compounds occur in the volatile bases obtained from hæmine appear to be the following: phyllopyrrole, 5 per cent.; hæmopyrrole and cryptopyrrole, about 20 per cent.

Piloty and Stock[48] suggest that in view of the complexity of the hæmopyrrole-phyllopyrrole mixture it would be preferable to call all the constituents by the general name hæmopyrrole, distinguishing them from each other by the suffixes *-a*, *-b*, etc., in the order of their melting points. Thus, Willstätter and Asahina's *iso*hæmopyrrole would be termed hæmopyrrole-*b*. According to Piloty and Stock, Willstätter and Asahina's hæmopyrrole is a mixture of two substances to which they have given the names hæmopyrrole-*b* and hæmopyrrole-*c* according to the suggested nomenclature. There are thus four hæmopyrroles (*a*, *b*, *c*, and *d*); the first of these is 3-methyl-4-ethylpyrrole; the second is Willstätter and Asahina's *iso*hæmopyrrole; the third is identical with a compound, 3:5-dimethyl-4-ethylpyrrole, which has been synthesised by Knorr and Hess[49]; whilst the fourth is phyllopyrrole.

A considerable number of other papers in this branch of the subject have appeared.[50]

[48] *Annalen*, 1912, **392**, 215; *A.*, i, 923.

[49] *Ber.*, 1911, **44**, 2758; *A.*, 1911, i, 1019.

[50] Leyko and Marchlewski, *Bull. Acad. Sci. Cracow*, 1911, A, 345; *A.*, i, 56; Willstätter and Asahina, *Ber.*, 1911, **44**, 3707; *A.*, i, 127; Grabowski and Marchlewski; *Ber.*, 1912, **45**, 453; *A.*, i, 297; Knorr and Hess, *Ber.*, 1912, **45**, 2626; *A.*, i, 900; Marchlewski, *Zeitsch. physiol. Chem.*, 1912, **79**, 351; *A.*, i, 646; Marchlewski and Grabowski, *Zeitsch. physiol. Chem.*, 1912, **81**, 86; *A.*, i, 1015.

The Colouring Matter of the Blood.

Closely connected with the chlorophyll question is the problem of the colouring matter of the blood; and as this seems to be within a few steps of its complete solution, a short summary of its later stages may be given here.

The colouring matter of the blood is composed of two portions, one of which is albuminous and is called globin, whilst the other is non-albuminous in character, and is termed hæmatin. It is with the latter part that we have to concern ourselves. In the body, it is supposed that hæmatin forms the source from which another substance, bilirubin, is produced; and the latter is one of the constituents of bile.

Now when hæmatin is reduced with hydriodic acid and phosphonium iodide, a series of four principal products is produced, namely, (1) a mixture of hæmopyrroles, (2) xanthopyrrolecarboxylic acid, (3) phonopyrrolecarboxylic acid, and (4) hæmatopyrrolidinic acid.[51] (See the scheme on p. 172.) Investigation of the hæmatin structure on this line has been hindered by the fact that hæmatopyrrolidinic acid is an amorphous substance which cannot be crystallised, and hence it has been impossible to make certain of its constitution. Now, at this point we are aided by the connexion between bilirubin and hæmatin. In view of their close relation in the body,[52] it seems reasonable to assume that there may be a certain relationship in structure between them[53]; and this idea is strengthened by an examination of their behaviour under the action of various reagents. When hæmatin is treated with acid, it yields a substance, hæmatoporphorin, which has the same composition as bilirubin, namely, $C_{16}H_{18}O_3N_2$. When these two latter substances are fused with potassium hydroxide, they yield closely analogous products,[54] of which the bilirubin derivatives are simpler than those obtained from hæmatoporphorin; the former substance gives rise to four pyrrole compounds, whilst the latter produces only two.

Now, when bilirubin is reduced with hydriodic acid and phosphonium iodide, it yields a substance, bilic acid, which differs in composition from the amorphous hæmatopyrrolidinic acid by only one oxygen atom: hæmatopyrrolidinic acid has the composition $C_{17}H_{26}O_2N_2$, whilst bilic acid is represented by $C_{17}H_{26}O_3N_2$.

[51] Piloty and Dormann, *Annalen*, 1912, **388**, 313; *A.*, i, 519.

[52] Küster, *Zeitsch. physiol. Chem.*, 1909, **59**, 63; *A.*, 1909, i, 319.

[53] It must be noted, however, that this is only an assumption, as in many cases one compound is transformed into another in the body by a series of decompositions and syntheses which leave very little of the original structure in existence.

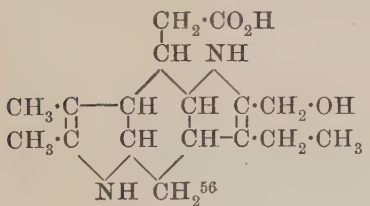
[54] Piloty and Thannhauser, *Annalen*, 1912, **390**, 191; *A.*, i, 736.

The chief point of practical interest, however, is that bilic acid is a substance of a crystalline character in contradistinction from the amorphous analogue. An investigation of the properties of bilic acid is therefore much more certain of results than an examination of the other compound.

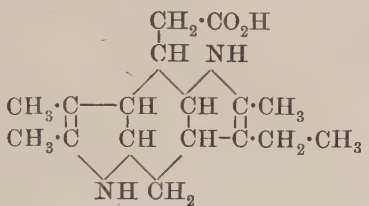
Let us now compare the effects of various reagents on these two substances. Both dissolve in warm water, giving a foamy liquid; neither crystallises out on cooling; but both may be salted out with sodium chloride. Both have the faculty of holding pyrrole derivatives in loose combination (adsorption); and both give amorphous metallic salts or picrates. When they are fused with potassium hydroxide, both give similar decomposition products, although in the case of bilic acid no hæmopyrrole is obtained. On oxidation with chromic and sulphuric acids, both produce hæmatic acid and methylethylmaleinimide.

The main difference between the two compounds, then, is that hæmatopyrrolidinic acid has one oxygen atom less than bilic acid; whilst bilic acid on fusion produces no hæmopyrrole fission products like those obtained from hæmatopyrrolidinic acid.

Piloty and Thannhauser[55] suggest that the following formula (I) is the most probable one to express the behaviour of bilic acid; whilst (II) would satisfy the necessities in the case of hæmatopyrrolidinic acid:

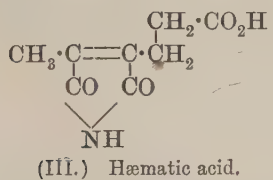


(I.) Bilic acid.

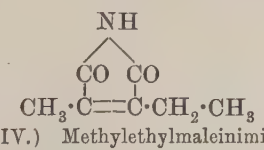


(II.) Hæmatopyrrolidinic acid.

The production of hæmatic acid (III) and methylethylmaleinimide (IV) from both (I) and (II) can be realised by an inspection of the formulæ; and it will be observed that the presence of the third oxygen atom in bilic acid in the centre of an alcoholic radicle would sufficiently explain the lack of hæmopyrroles in the fission



(III.) Hæmatic acid.



(IV.) Methylethylmaleinimide.

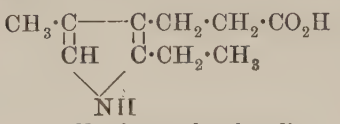
[55] *Annalen*, 1912, **390**, 191; *A.*, i, 736.

[56] It seems possible that this group and the ethyl radicle should be interchanged.

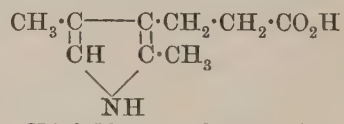
products of the former substance under the somewhat trying conditions of an alkali fusion.

Let us now turn back once more to hæmatin. On treatment with acids, this substance undergoes a change in the course of which it loses its iron content and is converted into hæmatoporphorin; and on reducing this last substance we get a mixture of hæmopyrroles, some hæmatopyrrolidinic acid, phonopyrrolecarboxylic acid, and xanthopyrrolecarboxylic acid. When treated by similar methods, bilirubin produces, among other substances, *iso*phonopyrrolecarboxylic acid, which is isomeric with phonopyrrolecarboxylic acid.

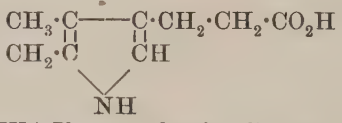
Xanthopyrrolecarboxylic acid[57] has been shown to have (probably) the structure I; and since *iso*phonopyrrolecarboxylic acid and xanthopyrrolecarboxylic acid on treatment with nitrous acid both yield the same semi-oxime,[58] it appears that *iso*phonopyrrolecarboxylic acid may be the homologue (II). Phonopyrrolecarboxylic acid probably has the structure represented by III:



(I.) Xanthopyrrolecarboxylic acid.

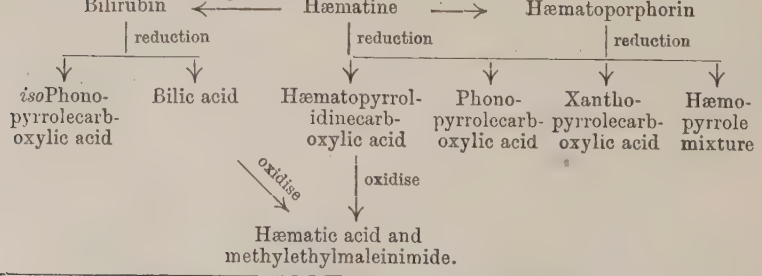


(II.) *iso*Phonopyrrolecarboxylic acid.



(III.) Phonopyrrolecarboxylic acid.

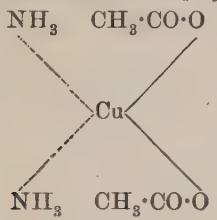
The following scheme shows some of the chief relationships between the principal compounds in this group:



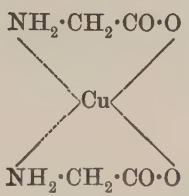
[57] Piloty and Dormann, *Annalen*, 1912, **388**, 313; *A.*, i, 519.
[58] Piloty and Thannhauser, *ibid.*, 1912, **390**, 191; *A.*, i, 736.

Complex Salts.

In recent years a considerable amount of attention has been directed to the question of complex salts, and a short section on this subject may not be misplaced in the present report, as apparently such compounds should be regarded as coming within the group of heterocyclic substances. It is well known that the copper salt of glycine possesses a brilliant blue tint, even more marked than the ordinary copper salts' colour, and seeming more akin to the blue solution obtained by dissolving a copper salt in excess of ammonia. Now, copper acetate has been found capable of adding on two molecules of ammonia to form a deep blue compound, the colour of which resembles that of the glycine copper salt, and the assumption is currently made that these two molecules of ammonia are directly attached to the copper atom by "auxiliary valencies" so that the formula of the compound may be written as in (I) if we designate the auxiliary valencies by dotted lines. On a similar assumption, the formula for the copper salt of glycine would be written as in (II).



(I)



(II)

During the current year, a considerable amount of work[59] has been done in this section of the field. An important class of compounds which has been fully studied in this connexion includes those which give the biuret reaction. The peculiar tint obtained when substances respond to this reaction is now ascribed to the formation of a complex copper or nickel salt; and the structural conditions necessary to the production of such a salt have been very fully dealt with by Kober and Sugiura.[60] It was found that the colour produced in the biuret reaction depends on the constitution of the complex salt formed; substances containing one copper and two nitrogen atoms give a deep blue tint; those containing one copper and three nitrogen atoms show a semi-biuret colour of varying shade; substances which contain one copper and four nitrogen atoms give a red tinge. Thus, the dipeptides and

[59] Weinland and Büttner, *Zeitsch. anorg. Chem.*, 1912, **75**, 233; *A.*, i, 530; Costăchescu, *Ann. Sci. Univ. Jassy*, 1912, **7**, 87; *A.*, i, 493; Costăchescu and Spacu, *ibid.*, 132; *A.*, i, 494; Ley and Ficken, *Ber.*, 1912, **45**, 377; *A.*, i, 243; Ley and Winkler, *ibid.*, 372; *A.*, i, 243.

[60] *J. Biol. Chem.*, 1912, **13**, 1; *Amer. Chem. J.*, 1912, **48**, 383; *A.*, i, 952, 953.

their carboxyl derivatives give a tint like glycine; tripeptides and their carboxyl derivatives (excluding their amides), and the amides of dipeptides give a semi-biuret tinge; whilst tetrapeptides and the amides of tripeptides give a purple-red colour in the biuret reaction. The further spectroscopic investigations in this direction will be of great interest when they are completed.

Miscellaneous.

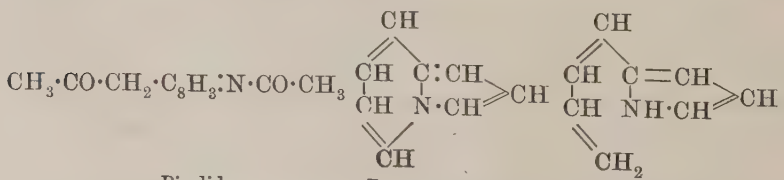
In the following paragraphs a few points will be considered which, although of interest, do not lend themselves to the more extended treatment which has been dealt out to the other subjects in this section of the report.

A new method of obtaining thiophen[61] has been devised which appears to give very good results. Acetylene is passed through an iron tube charged with pyrites, and so arranged that the used pyrites can be removed. The tube is heated to 300° while the gas is passed. On condensing the products, it is found that the yield contains 40 per cent. of thiophen; and on purification the substance can be obtained with a purity of 95 to 96 per cent. Compared with the usual methods, this new one seems to be eminently satisfactory especially from the point of view of cheapness.

A somewhat peculiar reaction between acetic anhydride and α-picoline has been described,[62] which may be expressed by the following equation:

$$C_6H_7N + 2(CH_3{\cdot}CO)_2O = C_{12}H_{11}O_2N + CH_3{\cdot}CO_2H + 2H_2O.$$

The nitrogen derivative thus obtained has no basic properties, reacts with hydroxylamine, phenylhydrazine, and semicarbazide, and condenses with two molecules of aromatic aldehydes, the products giving intensely coloured compounds with sulphuric acid. From the reaction with hydroxylamine, it is clear that the two oxygen atoms are true carbonyl oxygens, and are not acyl oxygens. When the substance is boiled with sulphuric or hydrochloric acid, it yields a base isomeric with indole, which, when reduced, takes up two atoms of hydrogen. The following names and formulæ are suggested for these compounds:



Picolide. Pyrrocoline. α-Butadienylpyrrole.

[61] W. Steinkopf, *Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 220; *A.*, i, 292.

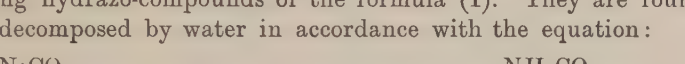
[62] Scholtz, *Ber.*, 1912, **45**, 734; *A.*, i, 385.

In the pyrazoline group, some investigations[63] have been begun with the view of obtaining derivatives of *cyclo*propane by the decomposition of pyrazoline compounds.

Azodicarboxylimide derivatives[64] of the formula (II), in which

(I.) (II.)

R is H, Ph, NH_2 or N:CHPh, have been prepared by the action of an ethereal solution of iodine on the silver salts of the corresponding hydrazo-compounds of the formula (I). They are found to be decomposed by water in accordance with the equation:



A continuation of the investigation of the *endo*azo-compounds[65] deserves notice, as the compounds described belong to the class of spiranes in which interest is being taken at the present time.

Some glyoxaline derivatives[66] allied to the alkaloid pilocarpine have been prepared, and their physiological effects have been tested.

Mention must also be made of the very extensive investigations of the pyrimidines[67] and hydantoins[68] which have been published during the year.

Molecular Asymmetry.

This subject was dealt with in last year's report.[1] Pope[2] has re-stated his views more explicitly this year, and gives the following definition, which seems to make his point of view clearer than before. "Every molecular configuration is enantiomorphous, and presumably capable of exhibiting optical activity, which contains no centre of symmetry; and, conversely, every molecular configuration is potentially optically inactive which contains a centre of sym-

[63] Kijner, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 165; *A.*, i, 245.

[64] Stollé, *Ber.*, 1912, **45**, 273; *A.*, i, 225.

[65] Duval, *Compt. rend.*, 1912, **154**, 780; *A.*, i, 398.

[66] Pyman, *T.*, 1912, **101**, 530.

[67] Johnson and Shepard, *Amer. Chem. J.*, 1912, **48**, 279; *A.*, i, 910; Johnson and Hill, *ibid.*, 296; *A.*, i, 912; Johnson and Moran, *ibid.*, 307; *A.*, i, 913.

[68] Johnson and Hoffman, *Amer., Chem, J.*, 1912, **47**, 20; *A.*, i, 136; Johnson and Guest, *ibid.*, 103, 242; *A.*, i, 316, 807; Johnson and Nicolet, *ibid.*, 459; *A.*, i, 585; Johnson and Ambler, *ibid.*, 197; *A.*, i, 799; Johnson, *J. Biol. Chem.*, 1912, **11**, 97; *A.*, i, 390; Johnson and Brautlecht, *ibid.*, 175; *A.*, i. 805; Johnson and O'Brien, *ibid.*, 205; *A.*, i, 806; Johnson, Pfau and Hodge, *J. Amer. Chem. Soc.*, 1912, **34**, 1041; *A.*, i, 807; Johnson and Nicolet, *ibid.*, 1048; *A.*, i, 808; Johnson and Bengis, *ibid.*, 1054, 1061; *A.*, i, 808, 809; Johnson and Chernoff, *ibid.*, 1208; *A.*, i, 810.

[1] *Ann. Report*, 1911, 71.

[2] Pope and Read, *T.*, 1912, **101**, 2325.

metry." The confusion appears to have arisen owing to the use of the expression "asymmetric atom" in a sense different from that in which this is usually employed. Pope's view is that in an enantiomorphous molecular configuration every atom present is asymmetric, in the sense that it is devoid of geometrical association with a centre of asymmetry.

In this connexion, attention may be drawn to the case of substances having the general formula:

$$\alpha\beta C\begin{matrix}\nearrow A\cdot B\\ \searrow B\cdot A\end{matrix}C\alpha\beta.$$

Such substances exist in *cis*- and *trans*-forms, and the *trans*-isomeride (internally compensated) possesses no element of symmetry other than a centre of symmetry, whilst the *cis*-forms (optically active) have no centre of symmetry, but possess a two-fold axis of symmetry. The case of the *cis*-1 : 4-diketo-2 : 5-dimethylpiperazines [3] furnishes the only example of this type which has been successfully examined up to the present. The same kind of asymmetry exists in the α- and β-2 : 5-dimethylpiperazines [4] which have recently been examined. Unfortunately, positive results were not obtained in this case; but the results of further experiments now in progress may increase our knowledge of this interesting class of isomerides.

A New Method of Resolving Inactive Mixtures into the Antipodes.

A few years ago [5] it was found that *d*-oxymethylenecamphor could be used as a reagent for determining whether a primary or secondary amine is externally or internally compensated. Oxymethylenecamphor in the enolic form has the structure represented by (I), and when it is allowed to condense with secondary amines it yields condensation products of the formula (II):

$$C_8H_{14}\begin{matrix}\nearrow C{:}CH\cdot OH\\ \searrow CO\end{matrix}\qquad C_8H_{14}\begin{matrix}\nearrow C{:}CH\cdot NX\\ \searrow CO\end{matrix}$$

(I.) (II.)

If the amine is internally compensated it yields only one product with *d*-oxymethylenecamphor; but two condensation products are formed by an externally compensated amine, and these can be separated by fractional crystallisation. In this way it is possible to ascertain whether the amine is potentially optically active or not; but the drawback to the method has hitherto been that the amine's two antipodic forms could not thus be obtained, as no

[3] Fischer, *Ber.*, 1905, **39**, 453; *A.*, 1906, i, 145; Fischer and Raske, *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 371; *A.*, 1906, i, 457; *Ber.*, 1906, **39**, 3981; *A.*, 1907, i, 18.

[4] Pope and Read, *loc. cit.*

[5] *Ibid.*, *T.*, 1909, **95**, 171.

method had been devised for splitting up the condensation product so as to liberate the amine portion. This defect has now been remedied,[6] for it has been shown that by acting on the condensation with bromine in carbon tetrachloride solution the hydrobromide of the base is obtainable.

Asymmetric Synthesis.

A considerable advance in the study of this subject has been made by the discovery[7] that an asymmetric synthesis can be brought about by the use of an optically active catalyst. When benzaldehyde and potassium cyanide are allowed to interact in solution, they yield racemic mandelonitrile; but if benzaldehyde is condensed with hydrocyanic acid in the presence of an optically active alkaloid, the resulting mandelonitrile is found to be optically active. The rotatory power of the product depends on the alkaloid employed; quinone produces a mandelonitrile which yields on hydrolysis *l*-mandelic acid, whereas quinidine favours the formation of *d*-mandelic acid. There appears to be no doubt that the alkaloid employed enters into combination with the cyanohydrins; and it also seems to be proved that the action of the alkaloids is a catalytic one, for the molar amounts of them necessary to produce the reactions are less than those of the products.

Racemism.

Very little work has been done in this division of the subject during the year. Jerusalem[8] has examined the crystallography of various active substances and the corresponding racemic forms, and finds that a close morphotropic relationship exists between them. Such a relationship follows from Barlow and Pope's theory, which thus receives further support.

The question of the existence of liquid racemates has been dealt with in the case of fused methyl racemate.[9] This work, which is based on the application of measurements of the velocity of crystallisation, the temperature-coefficient of the molecular surface energy, and the molecular heat of vaporisation, tends to prove that the fused substance is a mere mixture of the two antipodes, and not a true racemic compound.

The mechanism of the process of racemisation by heating has been examined,[10] and in the case of malic acid it has been shown

[6] Pope and Read, *T.*, 1912, **101**, 2325.
[7] Bredig and Fiske, *Biochem. Zeitsch.*, 1912, **46**, 7 ; *A.*, i, 983.
[8] *T.*, 1912, **101**, 1268.
[9] Gróh, *Ber.*, 1912, **45**, 1441 ; *A.*, i, 411.
[10] James and Jones, *T.*, 1912, **101**, 1158.

that fumaric acid is produced as an intermediate stage in the reaction. In the case of the racemisation of tartaric acid, considerable quantities of pyruvic acid were formed, and it is concluded that the following reversible reactions play a part in the mechanism:

$$CO_2H\cdot CH\cdot OH \rightleftharpoons CO_2H\cdot C\cdot OH \rightleftharpoons$$
$$CH(OH)\cdot CO_2H \qquad\qquad CH\cdot CO_2H$$

$$CO_2H\cdot CO \rightleftharpoons CO_2H\cdot CO + CO_2.$$
$$CH_2\cdot CO_2H \qquad\qquad CH_3$$

The Walden Inversion.

With the present year this problem appears to have entered a new stage. The full summary which was given in last year's report[11] renders it unnecessary to enter into much detail here; but a single example may be given to make the matter clear. If *d*-alanine is treated with nitrosyl bromide the main reaction product is *l*-α-bromopropionic acid, whereas if the *d*-alanine is esterified, the ester treated with nitrosyl bromide, and then hydrolysed, there is obtained *d*-α-bromopropionic acid; thus in each case the starting point is the same dextro-acid, but in one instance the final product is dextrorotatory, whilst in the other it is the optical antipode; and therefore at some point or other in the series of reactions there must have been a rearrangement of the groups around the asymmetric carbon atom.

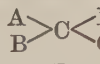
Hitherto, those investigators who have touched on the problem have confined their attention to this actual shifting of the groups in space, and have brought forward the views which were summarised last year. Now, however, it is beginning to be realised that there is another side to the question, namely, the actual mechanism of the reaction, apart from any spatial considerations. It will be well to take up these two points in the above order.

Biilmann[12] has examined the explanations put forward by Fischer[13] and by Werner,[14] and he considers that although at first sight they appear to amount to the same thing, yet on closer examination they are fundamentally different. In the first place, taking as his example the action of ammonia on α-bromopropionic acid, Fischer assumes that the ammonia molecule which reacts with the bromo-acid is dissociated into hydrogen and the amino-group; but Biilmann, basing his conclusions on the similarity of the actions of primary, secondary, and tertiary amines on bromo-compounds, regards this assumption as too great to be easily conceded, since,

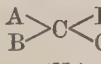
[11] *Ann. Report*, 1911, 60.
[12] *Annalen*, 1912, **388**, 330; *A.*, i, 420.
[13] *Ibid.*, 1911, **381**, 123; *A.*, 1911, i, 418.
[14] *Ber.*, 1911, **44**, 881; *A.*, 1911, i, 424.

according to him, it would entail the acceptance of the idea that tertiary amines also decomposed during such reactions.[15] Therefore, on his view, it is impossible to admit Fischer's contention that the amino-group simply takes the place left vacant by the ionised bromine atom. Secondly, to explain the optical inversion which takes place in the Walden change, Fischer assumes that in such cases the following phenomena occur: the bromine atom first becomes ionised, and is removed from the complex; then one of the remaining three groups attached to the asymmetric carbon atom moves into the place of the bromine atom; and, finally, the amino-radicle takes up the position left free by the shift of this group. As Biilmann points out, this forms a possible explanation of *how* the inversion occurs, but it merely carries us a step back, and leaves us still to discover *why* the groups should interchange their positions. In most cases it seems probable that, during the shifting of the groups from one position to another, racemisation would take place to an extent much greater than is observed in practice. These difficulties might be overcome if it were assumed that the ammonia molecule takes up a definite position sterically with regard to the other atoms concerned in the reaction; but in his paper Fischer expressly stated that he only assumed the attachment of the amino-group to the carbon atom by residual affinity "on the grounds of simplicity," and that such an attachment formed no part of the essentials of his hypothesis.[16]

Now, according to Biilmann, Werner's hypothesis differs from Fischer's at this critical point. Let us take a concrete example for the sake of clearness, namely, the action of hydrochloric acid on a substance of the formula (I), producing



(I.)



(II.)

a substance with the formula (II). Such a change could be assumed to occur in either of two ways, according as the hydrogen chloride molecule attaches itself to one side or other of the plane through ABD. If it attaches itself on the same side as the hydroxyl group, then, after water has been eliminated, the chlorine atom will occupy the same position as that of the original hydroxyl; if, on the other hand, the hydrogen chloride molecule attaches itself to the molecule on the side opposite to the hydroxyl, then the

[15] Mr. P. J. Brannigan has pointed out to me that a similar dissociation of the ammonia molecule is implicitly assumed in such reactions as amide formation and the production of aldehyde-ammonia; which seems to destroy the force of this part of Biilmann's argument.—A. W. S.

[16] Fischer (*Annalen*, 1912, **386**, i, 187) has stated that his paper was written "critically" rather than as a constructive explanation.

elimination of water will produce the mirror-image of the other chloro-derivative, and we shall have an example of Walden's inversion. Now Werner assumes this attachment of the hydrogen chloride molecule as part of his explanation; and if this be granted, it is clear that the deciding factor in the question will be the attractive forces exerted on the hydrogen chloride molecule by the various atoms which make up the compound ABCD·OH. The assumption of the existence of such forces is one which we can easily make, and from that the whole explanation of the Walden inversion follows naturally. If the attractive forces in question tend to bring the hydrogen chloride molecule and hydroxyl group to the same side of the plane ABD, then no inversion takes place; but if the tendency of these forces is to attract the hydrochloric acid to the opposite side of the optically active molecule the Walden change occurs.

Biilmann further suggests that racemisation might be considered as another case of intramolecular change analogous to the Walden inversion, in view of the influence which hydroxyl ions are known to exert on the former process. This suggestion, however, should be judged in connexion with the results of James and Jones in the racemisation of tartaric acid.[17]

Finally Gadamar's views may be mentioned.[18] He assumes that in such reactions as the Walden inversion an additive compound is primarily produced, which is formed by the new group attaching itself to the halogen atom instead of to the asymmetric carbon atom. When the inversion takes place in the compound CabcCl, the halogen atom is supposed to be removed from the carbon, leaving three groups behind. These then vibrate in such a way as to distribute themselves evenly about the carbon atom; but in the course of their movement they overshoot the equilibrium point, and thus pass into a position which is the mirror-image of the one previously occupied. The hydroxyl group then attaches itself to the carbon atom, and thus the inversion is accomplished. Gadamar assumes that the differing behaviour of the metallic hydroxides can best be explained by supposing that the normal hydrolysis is due to the action of the anion of the hydroxide, whilst abnormal results are due to the action of the cation. If this hypothesis were correct, it seems probable that the temperature of the reaction mixture would have a considerable influence on the amount of "overshooting" of the equilibrium position, and investigations in this direction would be of interest.

Turning now to the second problem, namely, the actual

[17] See p. 177.

[18] *Chem. Zeit.*, 1912, **36**, 1327; *A.*, i, 934.

mechanism of the reactions involved in the Walden inversion, we may begin by a summary of Biilmann's views. It is quite clear that in the case of the reactions of the bromo-substituted acids there are two possibilities: for if a given reagent reacts direct with the bromine atom, then we should expect a case of simple substitution; whereas if this is not the case, then we may have to deal with an intramolecular rearrangement in the course of the reaction. Let us examine from this point of view the case of the reactions of the halogen-substituted acids. Walden found that when *l*-chlorosuccinic acid is treated with potassium hydroxide, *d*-malic acid is formed; whereas when silver oxide is substituted for the alkali, *l*-malic acid is the principal product of the reaction. Now at first sight this appears strange, but a closer examination of the actual experimental conditions helps to clear up the difficulty. In most cases it appears that the reaction is not one between the halogen-substituted acid and silver oxide, but rather a mere decomposition of the silver salt; for instance, in the conversion of *l*-α-bromopropionic acid into *l*-lactic acid by this method, Fischer,[19] working at the ordinary temperature, shook together an aqueous solution of the acid and silver carbonate. The result of this, of course, would be the formation of the silver salt of *l*-α-bromopropionic acid, and since this substance itself in aqueous solution rapidly eliminates silver bromide, Biilmann doubts whether the excess of silver carbonate has any effect at all beyond neutralising the lactic acid which is formed as a final product; thus in this case we are not dealing with a simple interaction between silver oxide and the bromine ion of the acid (since the solution must be saturated with carbonic acid during the course of the reaction), and hence the case is not at all parallel to the interaction between the bromo-acid and potassium hydroxide.

On the basis of Senter's[20] investigations of the hydrolysis of halogen-substituted acids, Biilmann considers that, in the first place, the bromo-substituted acids ionise, and that in consequence of the negative charge on the acid ion the bromine atom becomes less firmly attached, and therefore more ready to react with the silver ions in the solution. The results of this series of changes may be expressed thus:

$$\begin{array}{l} CH_3 \\ CHBr \\ CO_2^- \end{array} + Ag^+ = \begin{array}{l} CH_3 \\ CH^+ \\ CO_2^- \end{array} + AgBr.$$

[19] *Ber.*, 1907, **40**, 503; *A.*, 1907, i, 192.

[20] *T.*, 1907, **91**, 460; 1909, **95**, 1827; 1910, **97**, 346; 1911, **99**, 95; *Zeitsch. physikal. Chem.*, 1910, **70**, 511; *A.*, 1910, ii, 276.

This "Zwitterion" then unites with a negative hydroxyl ion of water, forming an ion of lactic acid:

$$\begin{array}{l} CH_3 \\ CH^+ \\ CO_2^- \end{array} + OH^- = \begin{array}{l} CH_3 \\ CH{\cdot}OH. \\ CO_2^- \end{array}$$

Since we are dealing with ionic reactions throughout this process it is fair to assume that no change of relative position takes place in the groups around the asymmetric carbon, and hence no Walden inversion is observed. Similar arguments apply in the case of the action of nitrous acid on amino-acids, for it is known from analogy to the diazo-compounds that the nitrous acid first attaches itself to the nitrogen atom of the amino-group; so that in this case also we should expect to find simple substitution taking place without intramolecular rearrangement.

Another view of the interaction between bromo-substituted acids and alkali has been put forward by Holmberg.[21] From a study of the change in rotatory power, rate of elimination of bromine, and neutralisation with sodium carbonate in the case of *l*-bromosuccinic acid, he deduces that the following process occurs. The *l*-bromosuccinic ion breaks down rapidly into a bromine ion and an ion of propiolactonecarboxylic acid which is dextrorotatory. In neutral solution this lactone is only slowly hydrolysed; but as more and more malic acid is formed the hydrogen ion of this catalytically accelerates the process of hydrolysis; whilst at the same time it retards the rate of lactone formation. On these assumptions the process of the Walden inversion would be represented thus:

l-bromosuccinic acid $\longrightarrow$ *d*-malic acid lactone $\xrightarrow{KOH}$ *d*-malic acid.

Senter[22] points out that Holmberg's experimental data are confined to one dilution, and from his own results obtained at an earlier period he throws further light on the question. A solution of sodium bromoacetate was titrated at fixed intervals with sodium hydroxide and silver nitrate. In one case the acetate solution was $N/10$, in another it was $2N$ in strength. The results show that in the dilute solution the rates of formation of the bromine ion and the hydroxy-acid approximate closely to each other, and the reaction is one of the first order; but in the concentrated solution the velocity of bromine ion formation greatly exceeds that of acid formation, and the reaction in its first stages deviates more and more from the first order. Senter concludes that these results can best be interpreted by assuming that the mechanism of the reaction can be expressed by the following equations:

[21] *Ber.*, 1912, **45**, 1713, 2997; *A.*, i, 603, 948.
[22] *Ibid.*, 2318; *A.*, i, 828.

I. $CH_2Br{\cdot}CO_2Na + H_2O = CH_2(OH){\cdot}CO_2H + NaBr.$

II. $\left\{\begin{array}{l} CH_2Br{\cdot}CO_2Na + CH_2Br{\cdot}CO_2Na = \\ \qquad\qquad CH_2(O{\cdot}CO{\cdot}CH_2Br){\cdot}CO_2Na + NaBr. \\ CH_2(O{\cdot}CO{\cdot}CH_2Br){\cdot}CO_2Na + H_2O = \\ \qquad\qquad CH_2(OH){\cdot}CO_2H + CH_2Br{\cdot}CO_2Na. \end{array}\right.$

There is also a possibility of a third reaction leading to the formation of acetoxyacetic acid. In dilute solution, Senter supposes that the reaction is practically that which is represented by equation I, whilst in solutions of higher concentration the second reaction comes more and more into prominence. Senter considers that there is no evidence against the lactone formation assumed by Holmberg, but at the same time points out that he himself, in applying this very idea in his previous work, had assumed that such intermediate products would be very rapidly hydrolysed, and that there seems to be no reason for accepting the hypothesis that they would be very slowly decomposed under the given experimental conditions.

The Factors Influencing Optical Rotatory Power.

This field still attracts numerous investigators, and the data accumulated during the year testify to their unwearying industry. The subject, however, is complicated by so many obscure factors that it seems probable that a very long time will elapse before we are in a position to draw more than the most sketchy generalisations on the question of optical rotatory power regarded from the numerical point of view. Those interested in the development of the question will find a very complete summary of its more important branches in the Presidential Address.[23]

The work of the year has centred round the three main factors in the problem, namely, the effects of temperature, solvent and constitution, and the facts ascertained are very numerous. We must content ourselves with the briefest survey of the more interesting points. Taking the effect of temperature first, Pickard and Kenyon[24] have made a very exhaustive examination of the rotatory power in a series of optically active carbinols having the general formula $R{\cdot}CH(OH){\cdot}CH(CH_3)_2$, where R represents methyl, ethyl, etc., up to *n*-decyl. The investigation has been carried out over a wide range of temperature, extending at times up to 200°, and all except where experimental difficulties intervened, the rotation at the boiling point of the substances has been obtained, extrapolation being resorted to in a few instances. In the foregoing series it was found that the specific rotatory powers at 20° increase as the series is ascended until a maximum is reached with *iso*propyl-*n*-butyl-

[23] Frankland, *T.*, 1912, **101**, 658. [24] *Ibid.*, 620.

carbinol, after which the values decrease regularly to *iso*propyl-*n*-decylcarbinol. If we compare the values at the boiling point, however, we find that the members of the series from *n*-butyl to *n*-decyl have a constant value of $[M]_D + 29°$ (approximately); thus the values rise regularly until R is of greater mass than the *iso*propyl group in $R{\cdot}CH(OH){\cdot}CH(CH_3)_2$, and then become practically stationary.

In the course of an examination of various esters of di-trichloroacetyltartaric acid the occurrence of a minimum [25] in the rotation-temperature curves has been observed.

The influence of the solvent on the rotation of ethyl tartrate has been examined,[26] and certain relationships between the constitution of the solvent and its action on the rotatory power have been deduced; but to enter into these in detail would occupy too much space. The dependence of molecular rotatory power on the concentration of solutions of salts of *d*-camphor-β-sulphonic acid has been studied,[27] and it was found that the changes observed cannot be the result of the alteration of degree of electrolytic dissociation, but depend principally on the character of the metallic atom or electropositive grouping involved. Similar effects are produced by members of the same group in the periodic classification. The atomic weight does not appear to be an important factor.

In the Presidential Address,[28] Frankland drew attention to a possible cause of anomalies in rotatory power in homologous series. Since on the van't Hoff theory of the asymmetric carbon atom the ends of a straight carbon chain tend to approach one another when the chain contains five or six carbon atoms, it seems probable that such a state of things might affect optical rotatory power in some way, such as producing a maximum rotation when this critical length of chain was reached in a homologous series. Frankland quotes data which support his view, and the somewhat analogous results of Hilditch [29] reinforce his argument. Pickard and Kenyon,[30] however, state that the rotatory powers in the series examined by them do not agree with this conception; but as the problem is certain to be complicated to some extent by any branching in the chain, it seems best to regard the point as *sub judice* until more data are obtained which are free from complication.

In some of his previous work Hilditch [31] had established the importance of unsaturated groups as influences on optical rotatory

[25] Patterson and Davidson, *T.*, 1912, **101**, 374.
[26] Patterson and Stevenson, *ibid.*, 241. [27] Graham, *ibid.*, 746.
[28] *T.*, 1912, **101**, 658; compare *ibid.*, 1899, **75**, 368.
[29] *Ibid.*, 1909, **95**, 1581.
[30] *Ibid.*, 1912, **101**, 1428.
[31] *Ibid.*, 1909, **95**, 331, 1570, 1578; 1910, **97**, 1091; 1911, **99**, 224.

power, and from this he has been led to inquire [32] whether unsaturation may not be a factor in producing the irregularities in rotatory power which are sometimes observed among the lower members of series the higher members of which do not deviate to any marked extent from a constant rotatory power. The results obtained by Hilditch and Christopher appear to confirm this view. They have examined a series of menthyl esters of the α-bromo-aliphatic acids (in which the bromine atom is regarded as a centre of residual affinity), and they find that menthyl bromoacetate and menthyl α-bromopropionate possess rotatory powers markedly above the normal; the anomaly rapidly declines in the next members to a minimum, slightly sub-normal value; thereafter it rises to an approximately constant value when menthyl α-bromomyristate and α-bromopalmitate are reached. These investigations show that there are still other factors to be taken into account before one can arrive at any broad generalisation on the question of rotatory power and its connexion with chemical constitution; and it appears improbable that much progress will be made until an enormous mass of data has been accumulated. When this point is eventually reached, it seems evident that only a very clear thinker will be able to penetrate the maze of material at his command.

The Entropy Principle in Organic Chemistry.

Michael [33] has endeavoured to throw light on some of the more obscure points of stereochemistry by an application to them of the principle of entropy. His views may be very briefly summarised as follows: The factors which play a part in chemical reactions are: (1) the bound chemical energy of atoms already united, and (2) the free chemical energy which remains over after the union has taken place. Free chemical energy may be converted into bound chemical energy either by the direct union of atoms or by what is nowadays termed space-conjugation, that is, the influence on one another of atoms not directly united together in a chain. Now the conversion of free chemical energy into bound chemical energy is accompanied by a loss of energy in the form of heat, etc., so it is clear that when a compound has settled into its most stable chemical and spatial state the entropy will be at a maximum. Let us apply this to the question of stereoisomerides. It will be remembered that in cases like the tartaric acids van't Hoff in his theory of the asymmetric carbon atom postulated that the two central carbon atoms were free to rotate about their common axis, and, in order to avoid the deduction that in this way an innumerable

[32] *T.*, 1912, **101**, 192; Hilditch and Christopher, *ibid.*, 202.
[33] *Annalen*, 1912, **390**, 30; *A.*, i, 631.

series of isomeric tartaric acids might be capable of existence according to the relative positions in which the two groups $\cdot CH(OH)\cdot CO_2H$ stood, he was forced to make the further assumption that the various forces of attraction between the different atoms in the molecule tended to come into equilibrium in one particular favoured position. Now if we assume that the free chemical energy remaining in the groups $\cdot OH$, $\cdot CO_2H$, and H can equate itself through space, then some energy will be liberated in the form of heat, etc., at the time when the atoms pass into the position most favourable to this change. After this there may be slight oscillatory movement in the molecule, but free rotation of the carbon atoms will be impossible until heat is supplied to the system in quantities sufficient to reconvert the bound chemical energy thus lost into free chemical energy. It is evident that this view is perfectly general, and can be applied also to the case of geometrical isomerides of the ethylene type as well as to saturated compounds. Take the case of succinic acid and the corresponding unsaturated substances as an example. In succinic acid itself, according to Michael's view, the chemical resistance to rotation is small, and hence the *cis*-form passes into the stable *trans*-form with a marked increase in entropy. Now if two hydrogen atoms are removed from the *cis*-configuration of succinic acid (one from each methylene group) there is an increase in the bound chemical energy between the two central carbon atoms and also between the remaining hydrogen atoms and carboxyl groups. In this way the chemical hindrance to rotation is increased, which accounts for the greater stability of maleic acid as compared with the *cis*-form of succinic acid, and gives an explanation of the actual occurrence of maleic acid. Further, since the conversion of maleic acid into fumaric acid is accompanied by an increase of entropy, the free chemical energy of maleic acid will tend to bring about this conversion. With the aid of external energy supplied as heat, this transmutation becomes possible.

The catalytic action of hydrochloric acid on the maleic-fumaric transmutation is figured by Michael as follows: In the first place, a "polymolecule" of maleic acid and hydrochloric acid is formed. This contains more free energy than maleic acid alone, and consequently it is converted into the corresponding fumaroid "polymolecule." Then, since hydrochloric acid has a greater affinity for maleic than for fumaric acid, the fumaroid "polymolecule" reacts with maleic acid, giving fumaric acid and a fresh maleic-hydrochloric acid "polymolecule," so that the process continues until all the maleic acid has been converted into fumaric acid.

The Properties and Reactions of cis-trans-*Stereoisomerides.*

A portion of the Presidential Address of this year [34] was devoted to a consideration of the problems involved in the addition reactions of ethylenic stereoisomerides. It is a well-known fact that in many cases where we should expect to find two bromine atoms attaching themselves to a double or triple bond on the same side of the molecule, we actually get in practice a *trans*-addition, that is, one bromine atom is attached to one side of the molecule, whilst the second atom becomes fixed to the opposite side; thus, for example, the action of bromine on maleic acid produces *iso*-dibromosuccinic acid, which has now conclusively been shown to be the racemic form [35]; whereas, if *cis*-addition took place we should expect to find the internally compensated isomeride produced. Frankland has discussed the various cases which have arisen, and criticises Pfeiffer's hypothesis [36] to account for the phenomena. (In this connexion it may be pointed out that van't Hoff [37] had already brought grave objections against Pfeiffer's ideas.) Frankland's own explanation of the matter is so simple that one can only wonder why it was not put forward at an earlier period. If we are dealing with the relations of atoms in space, it seems inconsistent not to carry the deductions out thoroughly, and Frankland therefore takes into consideration the steric relations of the bromine molecule as well as those of the ethylenic or acetylenic compound under discussion. If we assume that in the bromine molecule the two atoms are separated by a distance which is sufficient to bring them to opposite sides of, say, a maleic acid molecule, then *trans*-addition is obviously the most probable process, since steric considerations would be against their coming into a position suitable for addition in the *cis*-position. This suggestion appears to clear up much of what was previously obscure.

Our knowledge of the physical properties of geometrical isomerides is very scanty; for although it seems probable that valuable results might be obtained by a systematic survey of the field, very few workers have gone far enough into it to provide us with material sufficient for generalisation. In one direction this defect has been remedied by a very complete series of determinations of the viscosities of various pairs of stereoisomerides of this type.[38] For the sake of convenience we may term "adjacent" all the isomerides of the *cis*-, *syn*-, and α-types, whilst the *trans*-, *anti*-, and β-isomerides are classed as "opposed." Thole has shown that

[34] *T.*, 1912, **101**, 673.
[35] McKenzie, *ibid.*, 1196.
[36] *Zeitsch. physikal. Chem.*, 1904, **48**, 40; *A.*, 1904, ii, 525.
[37] "Die Lagerung der Atome in Raume," 3 Aufl., 1908, p. 103.
[38] Thole, *T.*, 1912, **101**, 552.

acids and esters differ from one another as regards viscosity relations; for the adjacent acids are less viscous than the opposed isomerides, whilst with the corresponding esters these relations are reversed. The oximes examined, with one exception (benzilmonoxime), gave results parallel to those obtained with the acids, whilst the phenylhydrazones appeared to give anomalous readings, and in addition their configurations have not been determined with any certainty.

These results led Thole to the conclusion that, of two compounds the constituent radicles of which possess small residual affinity, the opposed isomeride has the lower viscosity. This may be ascribed to the tendency to potential ring-formation which usually exists in the adjacent isomerides, since such a condition notably enhances viscosity values. In compounds which possess greater residual affinity, this factor is masked by the intramolecular neutralisation of the residual affinities, which results in inhibition of molecular association, and hence leads to a depression of viscosity. It would be interesting to know, in view of these results, whether the spatial conjugation of unsaturated groups which have no tendency to ring-formation would affect viscosity to any great extent.

The Transmutation of cis-trans-*Stereoisomerides.*

One or two points of interest have arisen in this section of the subject. In his examination of the conversion of maleic into fumaric acid, Skraup [39] discovered that if hydrogen sulphide and sulphur dioxide were allowed to interact in a solution of maleic acid, fumaric acid was produced; but that no such change in the maleic acid took place if it were added to the solution after the reaction between the other two substances had run its course; nor was maleic acid affected by the presence of hydrogen sulphide or sulphur dioxide singly. On these phenomena he based his "resonance" hypothesis of transmutation, in which he assumed that every reaction produces waves in the ether which are capable of setting in motion other reactions which are "in tune" with the first. This problem has been taken up by Tanatar [40] in a somewhat similar set of reactions. Since in the Skraup reactions sulphur separates from the solution, Tanatar examined the action of sulphur on maleic acid. No effect was detected in the case of milk of sulphur or with the sulphur produced when ferric chloride and hydrogen sulphide are allowed to interact in the presence of maleic acid. The action of mineral acids on sodium thiosulphate was then tested, and it was

[39] *Monatsh.*, 1891, **12**, 146; *A.*, 1891, 1338.

[40] *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1742; *A.*, i, 160; Tanatar and Voljansky, *ibid.*, 1912, **44**, 1320; *A.*, i, 941.

found that the presence of maleic acid prevents the normal separation of sulphur, whilst at the same time the maleic acid is converted into its stereoisomeride. It was further observed that the presence of a mineral acid is unnecessary to produce the transmutation, for maleic acid in presence of sodium thiosulphate alone is converted into fumaric acid. Tanatar concludes from this that in the latter reaction some product is formed which causes the transmutation, and this view makes it unnecessary to assume any "resonance" phenomena.

The action of ultraviolet light on various stereoisomerides has been studied,[41] and it is found that the results obtained are not by any means uniform. The influence of constitution appears to be strongly marked, as can be seen from a comparison of the results obtained with the *o*-, *m*-, and *p*-forms of phenylnitrocinnamic acid. The *o*-compound melting at 196° yields traces of the isomeride melting at 147°; the *m*-derivative melting at 181° is partly and slowly changed into the isomeride melting at 195°, but the reverse change also takes place; whilst the *p*-compound, melting at 143°, is completely transformed into its isomeride, which melts at 214°.

A new exception to accepted views seems to have been discovered in the case of a second form of oleic acid[42] by keeping a specimen of ordinary oleic acid for some time at a temperature of 8—10°. Including this new variety (which may, however, differ merely in crystalline form from the others), it appears that we now know of four isomerides in the oleic series, whilst the current stereochemical views only allow for two. It is possible that this might be better explained under Michael's assumptions (compare p. 185).

The third isomeride of the erucic acid group, namely, *iso*erucic acid,[43] has been examined, and it was shown that it can be prepared by simply boiling brassidic acid in alcoholic solution with animal charcoal. Its absorption spectrum was found to be different from those of the other two isomerides, so there appears to be no doubt that it is actually chemically individual. Attention might be directed to these cases which form exceptions to the accepted views.

The method devised by Patterson and McMillan[44] has been applied to the question of the influence of solvent action on the velocity of transmutation in the case of oximes.[45] In its essentials, this method consists in dissolving the oxime in ethyl tartrate and noting the change in the rotatory power of the solution, which is

[41] Bakunin, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1911 [iii], **17**, 372; *A.*, i, 356; Stoermer and Heymann, *Ber.*, 1912, **45**, 3099; *A.*, i, 974.

[42] Kirschner, *Zeitsch. physikal. Chem.*, 1912, **79**, 759; *A.*, i, 533.

[43] Macbeth and Stewart, *P.*, 1912, **28**, 68.

[44] *T.*, 1907, **91**, 504.

[45] Patterson and Montgomerie, *ibid.*, 1912, **101**, 36, 2100.

brought about by the change of the oxime from one isomeric form into the other. If a neutral liquid be added to the solution of the oxime in ethyl tartrate, the effect of this third substance on the rate of oxime transmutation can be deduced from the polarimetric readings. In this way the influence of a large number of substances has been tested; for example, it is found that the following compounds affect the reaction's velocity in the order given, the velocity-constant being highest in the case of benzene: benzene, nitrobenzene, *p*-xylene, *m*-xylene, toluene, *o*-xylene, and mesitylene. In the case of the aliphatic alcohols the velocity constant decreases as the series is ascended, methyl alcohol showing most influence. The chief advantage of the method appears to be that the effect can be traced even when comparatively small proportions of the inert solvent are present in the reaction mixture.

Esterification and Hydrolysis Reactions.

As is the case in other fields, the problem of residual affinity has in recent years forced itself into the region of steric hindrance; and it is generally recognised by workers in this subject that a new factor has to be taken into account in their investigations. It is now assumed that in such a process as esterification, for instance, we have to take into account not only the spatial relations of the groups involved in the reaction, but also their residual affinity and its distribution within the molecule. If these two factors remained constant, there would be little difficulty in apportioning its due influence to each; but unfortunately they appear to vary with the conditions of experiment, and thus anomalous results are often obtained; for example, if we esterify acetic and trichloroacetic acids by the direct method (heating with alcohol) the latter acid esterifies more rapidly than the parent substance; but when the two are esterified catalytically (by being allowed to react with alcohol in the presence of hydrochloric acid) then the reaction velocities are reversed, and the parent substance forms an ester more rapidly than does the chloro-derivative. Thomas and Sudborough[46] have explained this apparent anomaly very simply, by assuming that both cases are catalytic processes, but in the direct esterification autocatalysis takes place, the acid acting as its own catalyst. If this be the case, then the stronger acid, trichloroacetic, should be a better catalyst than the weaker acetic acid, whereas in the presence of the much more active catalyst, hydrochloric acid, this advantage is lost and the purely spatial factors come into play.

With the view of testing this explanation, these authors have examined many acids which had already been studied by the cata-

[46] *T.*, 1912, **101**, 317.

lytic method; and their results certainly point to their explanation being correct. If the strengths of two acids (for example, a saturated one and its unsaturated analogue, which vary markedly from each other in the catalytic result) differ but little from each other, very little difference is observed in their esterification velocities when determined autocatalytically. In this case, the spatial factor appears to be the deciding one. When, however, this factor is overborne by the great difference between the strengths of the two acids, the stronger acid is much more rapidly esterified than the other, although this is not the case when both acids react under the influence of a catalyst much stronger than either, for in the latter instance the spatial factor is again the deciding one.

In the esterification of the ketonic acids, Sudborough [47] has found that a carbonyl group in the α-position to the carboxyl group has a marked retarding influence on the esterification velocity. In order to bring these results into line with the fact that the carbonyl group of ethyl pyruvate was found by Stewart and Baly [48] to be abnormally reactive, Sudborough puts forward an hypothesis with regard to the structure of the carboxyl radicle. He assumes that in the carboxyl group the hydrogen atom is not attached permanently to either oxygen atom, but oscillates from one to the other, so that the change shown below is continually taking place:

$$-C\begin{matrix}OH\\ \diagdown\!\!\diagup\\ O\end{matrix} \rightleftharpoons -C\begin{matrix}O\\ \diagdown\!\!\diagup\\ OH\end{matrix}.$$

Such a rearrangement would produce a highly reactive hydrogen atom, and would account for the fact that the hydrogen atoms of carboxyl groups are more reactive than those of alcoholic or phenolic hydroxyl groups. On the other hand, when we come to consider the rearrangement of valencies between the carbonyl groups postulated by Stewart and Baly:

$$CH_3\cdot\overset{\overset{O}{\|}}{C}\cdot\overset{\overset{O}{\|}}{C}\cdot OH \qquad\qquad CH_3\cdot\overset{\overset{O}{|}}{C}:\overset{\overset{O}{|}}{C}\cdot OH$$

it is clear that this could only take place at the expense of the change assumed by Sudborough, so that although the ketonic carbonyl group would have an enhanced reactivity, the carboxylic group would decrease in reactive power. Sudborough's suggestions seem to fit the case very well, and it might be pointed out that they could, with very little modification, be brought into line with the work of Miss Smedley,[49] so that they are not devoid of support in a totally different field.

The esterification velocities of various polybasic aromatic acids [50]

[47] *T.*, 1912, **101**, 1227. [48] *Ibid.*, 1906, **89**, 489. [49] *Ibid.*, 1909, **95**, 231.

[50] Wegscheider and Faltis, *Monatsh.*, 1912, **33**, 185; Wegscheider and Black, *ibid.*, 207; *A.*, i, 463; Wegscheider and Müller, *ibid.*, 1912, **34**, 899; *A.*, i, 771.

have been studied, and the rates of hydrolysis of various esters of substituted fatty acids [51] have also been examined. The results in the latter case show that esters of halogen substituted acids are much more slowly hydrolysed than those of the parent acid.

On re-reading the few pages of this report and comparing them with the volume of the papers published during the year, the author feels only too conscious that much of importance has been omitted, and that many subjects have been very cursorily treated. Not a few researches have been passed over on the ground that justice could be done to them only by entering into details which would have necessitated sacrifice of space which could ill be spared; whilst others have been left out because it seemed probable that further investigations would bring out clearer conclusions which could safely be left to the hands of later reporters when the subject has come into better perspective. At the same time, it is hoped that the main lines of progress during the year have been indicated, if not fully described, and that a fair survey of the field has been given. If this has been even partly accomplished, the author has been more successful in the task set him than he anticipated when he was engaged in collecting the material on which this report is based.

A. W. Stewart.

[51] Drushel, *Amer. J. Sci.*, 1912, [iv], **34**, 69; *A.*, i, 599.

ANALYTICAL CHEMISTRY.

This report follows the same general plan as that of last year, and, if the plan is not immediately obvious, the brevity of the report makes unnecessary any long explanatory introduction. It may be said, however, that the metals are grouped as they group themselves in the mind of an analyst rather than by reference to Mendeléeff's table, whilst in the short section relating to organic analysis the general arrangement is the same as that adopted in earlier reports, but without cross-headings, which give an appearance of exhaustiveness to which this report does not pretend. That the division of space between organic and inorganic analysis would be unequal was clear to the writer before he finally arranged his notes; the inequality could easily have been redressed, but only, in the writer's opinion, by omitting more interesting for less interesting matter. Apology is scarcely needed for giving rather extended reference to one or two matters of importance to analysts with commercial interests and to some departmental inactivities.

General.

A new and interesting application of precise thermometry to quantitative analysis has been made. The method depends on the observation of the precise temperature at which a solution attains the same density as a given, previously calibrated float, and its application is, of course, limited to cases where not more than one substance, in addition to the solvent, is present. Since the temperature of floating equilibrium is an almost linear function of the concentration, when a few points on the curve connecting the two variables have been determined, the concentration of an unknown solution may be deduced from the temperature at which the calibrated float just sinks in it. Conversely, the method may be employed to calibrate thermometers by means of solutions of known concentration. The exact density of none of the solutions need be known, since the method depends only on differences of density. Lest it be thought that the method has no advantage over methods

which correlate concentration with actual density, the following numbers may be given. A particular float just sank in alcohol of 98·99 per cent. strength at 15·391°. On adding water so that the percentage of water in the alcohol was increased from 1·01 to 3·44 per cent., the temperature of floating equilibrium was 24·093°, and intermediate experiments showed that the increase of temperature of floating equilibrium was very nearly a linear function of the concentration of water.[1] Since the float employed was so sensitive that the temperature at which it sank or rose could be determined within 0·001°, a simple calculation shows that the experimental error of the method is only about one-tenth that of a method depending on the determination of the density of the spirit, with an accuracy of ± 5 units in the sixth decimal place, the highest degree of accuracy with which densities can be determined with reasonable rapidity. To obtain the greatest accuracy of which the method is capable, a thermostat capable of being adjusted to any needed temperature and of being kept there within 0·005° is necessary, and in this connexion reference may be made to a paper on the control of temperature in the operations of analytical chemistry,[2] which should not be overlooked by anyone who may have occasion to design buildings intended for use as laboratories.

Electric heating has been made use of in ebullioscopic determinations for many years, but Bigelow,[3] who first made use of it, pointed out that difficulties due to electrolysis would certainly be encountered if the method were extended to aqueous solutions, and Beckmann[4] described experiments which confirmed this view. Consideration might have convinced these authors that electrolysis could be avoided by choosing a heating coil of resistance so low that the necessary heat could be imparted to the liquid without the drop in potential across the coil exceeding some assigned quantity. That their general warning was unsound and their conclusions only valid for their own coils of relatively high resistance, has now been shown experimentally by two authors, who appear to have worked in ignorance of the work of Bigelow and Beckmann. The new apparatus owes its origin to difficulties encountered in the use of the ordinary Beckmann apparatus with substances of high molecular weight and sparing solubility, but it is said to possess the advantage that readings constant to 0·001° are obtained without special precautions, and its general use where the necessary current is available is to be expected.[5] Of less general interest, but impor-

[1] T. W. Richards and J. W. Shipley, *J. Amer. Chem. Soc.*, 1912, **34**, 599; *A.* ii, 599. [2] T. W. Richards, *8th Inter. Cong. Appl. Chem.*, 1912, **1**, 403.
[3] S. L. Bigelow, *Amer. Chem. J.*, 1899, **22**, 208; *A.*, 1900, ii, 9.
[4] E. Beckmann, *Zeitsch. physikal. Chem.*, 1908, **63**, 177; *A.*, 1908, ii, 663.
[5] E. Knecht and J. P. Batey, *T.*, 1912, **101**, 1189.

tant in view of the very considerable difficulties which its authors have overcome, is an apparatus for ebullioscopic determinations at temperatures from $-36°$ to $-83°$ with solvents such as hydrogen sulphide, chloride, bromide, and iodide.[6]

The work of Thorpe and Rodger is proof that so long ago as 1894 it was possible to measure viscosities with great exactness.[7] Yet until recently viscosities of oils have been generally measured in analytical laboratories by one or other of the commercial instruments which are quite unsuitable for scientific research, although possessing an ease of manipulation very desirable in such work. More rarely use has been made of Ostwald's viscometer, which is much easier to set up than Thorpe and Rodger's "glischrometer," an instrument which demands much preliminary work, whilst the measurements themselves are much more complicated than with the Ostwald type of instrument with vertical capillary. Several investigations made within the last few years have, however, pointed to the fact that the Ostwald type of instrument holds serious sources of error, by far the greatest arising from the fact that no correction is made for the kinetic energy imparted to the liquid on entering the capillary,[8] that is to say, for the term $vd/8\pi lt$ in Pouseuille's formula $\eta=\pi r^4pt/8lv-vd/8\pi lt$. In the course of an investigation on the viscosity of emulsions, the authors found it possible to simplify the apparatus[9] of Thorpe and Rodger, and one of them has since described a still further modified form of instrument, which marks a very great advance, not in precision of viscometry —in point of precision the work of Thorpe and Rodger left nothing to be desired—but in the ease and rapidity with which viscosities may be measured with a degree of accuracy not far short of the highest attainable. The instrument is empirical only in the sense that it is so constructed that the exact dimensions of the capillary cannot be determined, and it must be standardised on some liquid of approximately the same viscosity as the liquids for which it is to be used, and of which the absolute viscosity is known. The general adoption of an instrument of this type in work on oils, always selecting a capillary of such dimensions that the kinetic energy correction was less than 0·5 per cent. of the total viscosity, would give a value to future numbers which few of those published up to the present possess. The extra demand on the analyst's time

[6] E. Beckmann and W. Weber, *Zeitsch. anorg. Chem.*, 1912, **74**, 297; *A.*, ii, 431.

[7] Sir T. E. Thorpe and J. W. Rodger, *Phil. Trans.*, 1894, **185**, A, 410.

[8] M. R. Schmidt, *Baltimore Dissertation*, 1909; E. C. Bingham and T. C. Durham, *Amer. Chem. J.*, 1911, **46**, 278; *A.*, 1911, ii, 968.

[9] E. C. Bingham and G. F. White, *J. Amer. Chem. Soc.*, 1911, **33**, 1257; *A.*, 1911, ii, 858.

as compared with the use of one of the commercial instruments is not very great, and the numbers obtained would be available for the purpose of correlating viscosities with other physical and chemical properties, whereas the numbers obtained by the commercial instruments and in many cases even by Ostwald's viscometer are insufficiently simply related to the true viscosities to be of any use for such a purpose.[10]

The most important improvements to be recorded in quantitative microchemical analysis are the construction of the beam and pointer of the Nernst balance in a single piece, with a glass counterpoise fused on to the beam at the end near the pointer, the substitution of spongy platinum for asbestos fibre in the construction of the Donau filter, and an ingenious arrangement for conducting precipitations and transferring the precipitate to the filter without loss.[11] A paper which describes the application of Carius' method to the determination of quantities of sulphur or halogens of the order of 1 milligram is perhaps deserving of notice even by those who have so far found no use for microchemical methods. Since 1 milligram of sulphur or halogen can be determined with an error well under 2 per cent., the use of somewhat larger quantities should give results of sufficient accuracy for many purposes, with greatly reduced risk of serious accident as compared with Carius' method as usually carried out, besides much saving of space, time, and glass.[12]

Gas Analysis.

Last year attention was directed to a new and accurate method for the estimation of nitric oxide in the presence of nitrous oxide, a problem which until that date had not found a satisfactory solution.[13] An entirely different method, but one which is said to be equally accurate, has since been described. It depends on Raschig's observation that the oxidation of nitric oxide proceeds in two stages, the first of which, corresponding with the formation of the trioxide, proceeds with great rapidity, whilst the second, corresponding with the formation of the tetroxide, requires an appreciable time for its completion. The method now described consists in oxidation of nitric oxide to nitrogen trioxide and absorption of the latter by potassium hydroxide in the form of sticks, the formation of any tetroxide being inhibited by confining the gas together with some potassium hydroxide over mercury, and then admitting a measured and sufficient volume of air. In this way the nitrogen

[10] G. F. White, *Biochem. Zeitsch.*, 1911, **37**, 482; *A.*, ii, 61; also *J. Ind. Eng. Chem.*, 1912, **4**, 106.

[11] J. Donau, *Monatsh.*, 1911, **32**, 1115; *A.*, ii, 199.

[12] *Ibid.*, 1912, **33**, 169; *A.*, ii, 384.

[13] *Ann. Report*, 1911, 156.

trioxide is transformed into potassium nitrite as fast as it is produced.[14]

A recent paper on the estimation of hydrogen and methane describes no new methods, of which there is already a wide choice, but it does offer very valuable suggestions in regard to four known methods. The author shows that the Drehschmidt capillary may be replaced by a quartz capillary containing a short length of platinum wire of such diameter that it nearly fills the tube, one advantage of the arrangement being that there is no risk of propagation of flame from the heated portion of the capillary to an explosive mixture contained in the gas burette to which it is connected. When using the Winkler-Dennis combustion pipette there is often difficulty in burning the last of the methane, so that the operation extends over a considerable period, during which such an amount of mercury may be oxidised as to give rise to serious error. This source of error may be avoided by enclosing the electrically-heated spiral in a quartz tube, which becomes the outer limb of the capillary U-tube of a simple mercury pipette. The gas is passed slowly to and fro between the burette and pipette over the heated spiral. It is shown that fractional combustion of hydrogen by means of palladium asbestos is successful only if the passage of the gas is slow and the temperature of 400° not exceeded, and an ingenious yet easily constructed device is described for controlling the temperature. Finally, the comparatively new method, depending on the absorption of hydrogen by means of a palladium sol, together with a soluble picrate,[15] is dealt with. Although it gives excellent results, as originally described, the method is rendered tedious by the persistent frothing of the liquid. The froth is instantly destroyed by a few drops of alcohol, but alcohol makes the reagent useless for further determinations. For this reason, and because the absorptive capacity of the reagent falls off somewhat rapidly on storage, even in the dark, the author has altered the whole technique of the method, which, as modified, is economical both of the analyst's time and of the expensive reagent.[16]

In 1910 a new interferometer was described, by means of which it was possible to solve simple problems of technical gas analysis. The authors confined themselves, however, to relatively simple problems, such as the determination of methane in mine air and the examination of technical hydrogen.[17] It has since been shown that the instrument may be used for the analysis of flue gases. In

[14] O. Baudisch and G. Klinger, *Ber.*, 1912, **45**, 3231 ; *A.*, 1913, ii, 74.

[15] C. Paal and W. Hartmann, *Ann. Report*, 1910, 160 ; also O. Brunck, *Chem. Zeit.*, 1910, **34**, 1313, 1331 ; *A.*, 1911, ii, 149.

[16] W. Hempel, *Zeitsch. angew. Chem.*, 1912, **25**, 1841 ; *A.*, ii, 987.

[17] Haber and Löwe, *ibid.*, 1910, **23**, 1393.

the absence of carbon monoxide, the results are exact, whilst the presence of that gas may be inferred if the sum of the percentages of oxygen and carbon dioxide is appreciably less than it should be, having regard to the composition of the fuel and to the excess of air above that necessary for combustion.[18]

Inorganic Analysis.

Qualitative.—Since the reference in the report for 1908 to the system of qualitative analysis devised by Noyes and Bray,[19] two further papers have appeared, one by each author. The earlier one dealt with the separation of the alkali earths and the members of the alkali group,[20] whilst the last deals with acidic constituents.[21] The whole series of papers occupies some two hundred pages, and, since they have not all appeared in the same journal, would be of much greater use if re-issued as a textbook of qualitative analysis. Necessarily these papers contain much that is familiar to everyone, but it is obvious that they embody an immense amount of original work. The number of new methods is so large that the authors are certain to incur the charge of unnecessarily multiplying methods, and analysts of the older school may be expected to express impatience of the detailed directions given, but the avowed object of the authors was to select or devise tests of known and roughly equal sensitiveness, and preference has been given to methods which enable the experienced analyst to form an approximate estimate of the quantities present. Such aims cannot be achieved without close attention to detail.

The writer does not share the enthusiasm for methods of qualitative analysis which circumvent the necessity for the use of hydrogen sulphide, because he finds a hydrogen sulphide apparatus indispensable for quantitative separations and for effecting reductions. The ingenuity which has been shown in avoiding the use of the gas, however, is sufficient, even if other evidence were lacking, to show that there are circumstances where an alternative method is desirable. Attention was directed last year to the work of Ebler in this connexion.[22] The year under review has witnessed the appearance of another comprehensive scheme by an author who makes no reference to Ebler or any other worker. No new reaction is made use of, so that it is possible to appraise the method roughly without trial, and it may be said that it might be expected to effect

[18] O. Mohr, *Zeitsch. angew. Chem.*, 1912, **25**, 1313.
[19] *Ann. Report*, 1908, 181.
[20] W. C. Bray, *Tech. Quart.* 1908, **21**, 450; *A.*, 1909, ii, 431.
[21] A. A. Noyes, *J. Amer. Chem. Soc.*, 1912, **34**, 609; *A.*, ii, 599.
[22] *Ann. Report*, 1911, 157

fairly sharp separations, whilst no unduly tedious operations are introduced.[23] It may be specially commended to the consideration of those who are impatient of lengthy descriptions. In yet another paper dealing with inorganic qualitative analysis as a whole, a large part is occupied with a description of a scheme which dispenses with the use of hydrogen sulphide.[24]

It has been shown that tetramethyldiaminodiphenylmethane, previously recommended as a reagent for the detection of lead and manganese,[25] is a very delicate reagent for gold, solutions containing 1 part of gold in 5 millions developing a distinct purple colour on treatment with it. The metals of the platinum group do not interfere.[26] A microchemical test for manganese, capable of detecting 0·005 milligram, has also been described,[27] but perhaps the most notable achievement in the domain of qualitative analysis has been the improvement in the well-known cobaltinitrite test for potassium, the sensitiveness of which has been increased a hundred-fold. The improvement consists in making the test in presence of silver nitrate, and depends on the much lower solubility of the double cobaltinitrites of potassium and silver as compared with that of potassium cobaltinitrite or sodium dipotassium cobaltinitrite. If the test is applied after removal of the heavy metals and of ammonium salts, nothing can interfere except rubidium, cæsium, and thallium, which will seldom be present in quantity where small amounts of potassium call for detection.[28]

Quantitative.—Chlorate is usually determined to-day by a direct iodometric method, but disagreement among different chemists has led to periodical proposals to return to the more troublesome distillation method of Bunsen. It has now been shown that the direct method is exact provided the chlorate be dissolved in air-free water and the hydrochloric acid used be also freed from air.[29] The exact determination of chlorite in admixture with chlorate, hypochlorite, and chloride is perhaps not a common problem, but should it arise a new gravimetric method depending on the insolubility of lead chlorite in 80 per cent. alcohol will prove useful, and greatly simplify the separate estimation of the other constituents of the mixture.[30]

[23] H. Trapp, *Zeitsch. anal. Chem.*, 1912, **51**, 475 ; *A.*, ii, 685.
[24] A. Purgotti, *Gazzetta*, 1912, **42**, ii, 58 ; *A.*, ii, 984.
[25] A. Trillat, *Compt. rend.*, 1903, **136**, 1205 ; *A.*, 1903, ii, 512.
[26] R. J. Carney, *J. Amer. Chem. Soc.*, 1912, **34**, 32 ; *A.*, ii, 298.
[27] M. Wagenaar, *Pharm. Weekblad*, 1911, **49**, 14 ; *A.*, ii, 206.
[28] L. L. Burgess and O. Kamm, *J. Amer. Chem. Soc.*, 1912, **34**, 652 ; *A.*, ii 604.
[29] A. Kolb, *Zeitsch. angew. Chem.*, 1912, **25**, 1168 ; also *Chem. Zeit.*, 1912, **36**, 635.
[30] G. Lasègue, *Bull. Soc. chim.*, 1912, [iv], **11**, 884 ; *A.*, ii, 988.

It has been shown that, in alkaline solution, the reaction:

$$N_2H_4 + 4K_3Fe(CN)_6 + 4KOH = 4N_2 + 4K_3Fe(CN)_6 + 4H_2O$$

is quantitative until either the whole of the hydrazine or the whole of the ferricyanide has disappeared, and on this reaction an exact gasometric method for the estimation of ferricyanide has been based.[31] The method is equally exact when applied to the estimation of hydrazine, but the technique is then somewhat complicated by the action of the excess of ferricyanide on the mercury used as confining liquid, so that, so far as the determination of hydrazine is concerned, the method scarcely challenges the iodine method of Stollé,[32] which leaves nothing to be desired.

Although there is no doubt that Feld's method for the estimation of ferrocyanide is capable of yielding accurate results in experienced hands, there is abundant evidence that the hands must be experienced, not merely capable, or, in other words, that the conditions which determine success in carrying out Feld's process have not yet been defined with sufficient exactness.[33] In these circumstances, a new method, apparently less dependent on the personal equation, is welcome. It depends on the fact that in presence of a small quantity of cuprous chloride and excess of sulphuric acid, all ferrocyanides—even insoluble ones—are decomposed with the evolution of the whole of their cyanogen as hydrogen cyanide, which may be distilled and determined in the usual manner. The simplicity of the method, which is shown to be exact, should recommend it even to those who are skilled in the use of Feld's method.[34]

The usual methods for the determination of fluorides are far from exact when very small quantities have to be estimated, and special methods which enable a food analyst to assert with confidence that an article contains not less than some stated proportion of fluorine, although useful to such analysts, are insufficiently exact for the purpose of those who are engaged in determining the distribution of fluorine in nature, whether it be in living tissues or in minerals of which fluorine is a minor constituent. Three papers dealing with the estimation of minute quantities of fluorine must therefore be accounted important, as they will undoubtedly give greater value to future statistical work of the kind mentioned.[35]

Having regard to the immense sums paid by chemical manufacturers for nitrate of soda, the value of which depends solely on its

[31] P. R. Rây and H. K. Sen, *Zeitsch. anorg. Chem.*, 1912, **76**, 380; *A.*, ii, 817.

[32] R. Stollé, *J. pr. Chem.*, 1902, [ii], **66**, 332; *A.*, 1903, ii, 100.

[33] *Ann. Report*, 1910, 164.

[34] H. E. Williams, *J. Soc. Chem. Ind.*, 1912, **31**, 468; *A.*, ii, 704.

[35] A. Gautier and P. Clausmann, *Compt. rend.*, 1912, **154**, 1469, 1670, 1753; *A.*, ii, 681, 805, 806.

nitrogen content, it is remarkable that it should still be paid for on the basis of analytical reports which, in their turn, are based on the determination of chloride and sulphate (calculated as sodium salt), moisture, and insoluble matter, and the subtraction of these percentages from 100. The method invariably overestimates the sodium nitrate, the average error being about 1 per cent., but it may reach 3 per cent. Not only do all samples contain soluble salts of calcium, magnesium, iron, and aluminium in small amount, but sodium perchlorate is occasionally present up to nearly 1 per cent., and the percentage of potassium nitrate may exceed 8 per cent. The suggestion made at the recent Congress of Applied Chemistry that the time has arrived for the general adoption of a direct method of valuing nitrate will commend itself to all chemists, and since the suggestion came from the spokesman of an important group of American consumers, it may have weight even with those who benefit by the present arrangement. There will be less unanimity among chemists concerning the particular method of analysis recommended, namely, reduction to ammonia in alkaline solution by means of Devarda metal and distillation from a very elaborate apparatus.[36]

A method for the estimation of nitrite, depending on the readiness with which nitrous acid is converted into its methyl ester, and the low boiling point of the latter ($-12°$), is worthy of note. The method affords a ready means of determining nitrite in presence of nitrate, and, although one may not agree with its authors that no other satisfactory method of effecting this separation exists, the simplicity and proved accuracy of the new method commend it. All that is necessary is to mix the neutral solution with excess of methyl alcohol and a known excessive quantity of acid, to bubble air through the mixture, and then titrate the remaining free acid with alkali.[37]

The observation that even a small fraction of a milligram of selenium per litre suffices to bring about rapid destruction of the liquors of sulphite cellulose factories, with production of sulphuric acid and gypsum,[38] has led to an investigation on the estimation of minute amounts of selenium in brimstone and pyrites. Brimstone is burned in a combustion tube in a current of air, an asbestos plug serving to catch all but an unweighable trace of the selenium which passes forward as a fog with the small quantity of sulphur trioxide which is always formed; the selenium is dissolved out of the tube by means of potassium cyanide, precipitated as dioxide,

[36] W. S. Allen, *8th. Inter. Cong. Appl. Chem.*, **1**, 19.

[37] W. M. Fischer and N. Steinbach, *Zeitsch. anorg. Chem.*, 1912, **78**, 134; *A.*, ii, 1093.

[38] P. Klason, *Verein. Zellstoff u. Papierchemiker*, 1909, 61.

freed by an ingenious device from traces of sulphur, and obtained as pure dioxide, which is then determined iodometrically.[39]

The work of Allen and Johnston on the exact determination of sulphate made our knowledge of the barium sulphate precipitation nearly complete,[40] but it did not provide an easy solution of the practical problem of valuing pyrites, the most important raw material of chemical industry. A method recently described, if it does not solve this problem, goes so far that it is likely to become and remain for some considerable time a standard method. Allen and Johnston's work made it appear unlikely that an exact method would be discovered, which would be generally applicable and require no correction, and yet not owe its accuracy to a compensation of errors. The new method is avowedly a compensation method, but it differs from earlier methods of this kind in having been worked out after and with full knowledge and appreciation of the work of Allen and Johnston. The "barium sulphate" as brought to the balance always contains barium chloride, but the proportion of this is never less than 0·27 per cent., nor more than 0·30 per cent., and so nearly balances the negative errors that the results are accurate to 0·05 per cent. How far we have travelled from textbook methods of determining sulphate will be appreciated from the statement that precipitation is made in the cold, that a Gooch crucible is used, and that the quantity of barium sulphate handled approximates 5 grams.[41] It should be added that the whole method is as simple as, if not simpler than, any method yet described for the valuation of pyrites.

A rapid yet exact method for the estimation of the free sulphur in spent oxide has long been wanted. A method recently described, depending on the conversion of the sulphur into sodium thiocyanate by digestion with an alcoholic solution of sodium cyanide and titration of the thiocyanate, is not only rapid but more exact than methods depending on the oxidation of the carbon disulphide extract and determination of the resulting sulphate because some of this sulphate may be derived from compounds of sulphur soluble in carbon disulphide, but useless to the sulphuric acid maker.[42]

Müller's benzidine method[43] for the volumetric estimation of sulphate has disappointed the expectations that were raised by its appearance and by Raschig's[44] early investigation of it. For the

[39] P. Klason, *Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 18, 1; No. 29, 1; *A.*, ii, 201, 990; *Zeitsch. angew. Chem.*, 1912, **25**, 514.

[40] *Ann. Report*, 1911, 159.

[41] W. S. Allen and H. B. Bishop, *8th. Inter. Cong. Appl. Chem.*, 1912, **1**, 33.

[42] C. Davis and J. L. Foucar, *J. Soc. Chem. Ind.*, 1912, **31**, 100; *A.*, ii, 384.

[43] W. Müller, *Ber.*, 1902, **35**, 1587; *A.*, 1902, ii, 425.

[44] F. Raschig, *Zeitch. angew. Chem.*, 1903, **16**, 617; *A.*, 1903, ii, 572.

routine analysis of a number of very similar samples it may sometimes be employed with a saving of time; but in other cases the necessary investigation to determine whether it is applicable occupies more time than a gravimetric determination. In many cases the composition of a solution is known within certain limits, and in such cases reference to two recent papers may inform the analyst at once whether the solution is one in which sulphate can be determined with tolerable exactness by means of benzidine.[45]

Although copper can now be estimated with a degree of exactness approaching that of a mint assay of gold bullion,[46] the analytical chemistry of copper and its ores is far from being a book the last page of which has been written. On the contrary, the number and value of papers dealing with the subject tend to increase, and some recent ones must be referred to. Rhead's method[47] for the titration of copper by means of titanous chloride has been greatly simplified, and shown to be as exact as a volumetric method can be.[48] A new gravimetric method, depending on the selective reducing action of hydroxylamine in presence of alkali tartrate, promises to be useful, since it is available in presence of antimony, zinc, bismuth, lead, iron, arsenic, and reasonable amounts of ammonia or nitrates.[49] The estimation of copper in pyrites has been simplified by the discovery that the *aqua regia* solution may be directly electrolysed if certain conditions, easily realised, are complied with.[50] A paper and discussion on the limits of accuracy attainable in copper and brass analysis must also be adjudged important, as it should lead to a diminution in the number of certificates disfigured by insignificant figures.[51] Such figures are not peculiar to reports on copper and brass, but extend to every branch of analytical chemistry, and raise a very grave question, which the profession as a whole will be compelled to consider unless amendment is more prompt than the present writer ventures to hope for. Finally, with regard to copper, attention must be directed to a paper on the determination of oxygen in refined copper. It was shown some time ago that the loss of weight on heating copper drillings in hydrogen is not due entirely to oxygen from cuprous oxide and sulphurous acid, but also includes gases derived by the metal from the fuel and other sources, and it is usual now to heat the drillings to constant weight in a current of carbon dioxide before proceeding

[45] K. K. Järvinen, *Ann. Acad. Sci. Fennicae*, A, **2**, 1910, No. 4; 1911, No. 16; *Chem. Zentr.*, 1912, i, 526; *A.*, ii, 486.

[46] *Ann. Report*, 1911, 168.

[47] *Ibid.*, 1906, 207.

[48] L. Moser, *Chem. Zeit.*, 1912, **36**, 1126; *A.*, ii, 1097.

[49] A. Bayer, *Zeitsch. anal. Chem.*, 1912, **51**, 729; *A.*, ii, 1212.

[50] W. D. Treadwell, *Chem. Zeit.*, 1912, **36**, 961; *A.*, ii, 998.

[51] E. A. Lewis, *J. Soc. Chem. Ind.*, 1912, **31**, 96.

to the determination of oxygen. It is now shown that similar treatment with carbon dioxide should follow the treatment with hydrogen, as copper may occlude so much hydrogen that an oxygen determination, as commonly practised, may be 20 per cent. in error.[52]

As every analytical chemist knows, the technique of the Marsh-Berzelius test for arsenic was greatly improved, and the method made very approximately quantitative in the years immediately succeeding the unfortunate epidemic of arsenical poisoning in 1901, and everyone who has occasion to determine small quantities of arsenic is now practised in this method. The recent statement that for purposes of works control the Marsh test was obsolete, because of its too great tedium and expense, would undoubtedly have encountered lively opposition had it not been the opening sentence of a paper which seems to establish the simpler Gutzeit test at last on a trustworthy basis. Since 1901 many authors have advocated the use of the Gutzeit test, but not even Sanger and Black,[53] on whose work the present authors have largely built, provided for the interfering effect of small quantities of iron, which are, or may be, present in so large a proportion of the substances which have to be tested for arsenic. The success and general applicability of the method now described depend mainly on the observation that ferrous iron *plus* a trace of stannous chloride actually increases the sensitiveness of the test, and to keep the conditions uniform, ferrous iron is added as a matter of routine.[54]

An unusual number of papers dealing with the estimation of glucinum have appeared within the year. Two volumetric methods, depending on the fact that glucina is so weak a base that solutions of its normal salts may be titrated with alkali hydroxide using phenolphthalein as indicator, or made to liberate iodine from a solution of iodide and iodate, have been described,[55] whilst the conditions which determine the quantitative precipitation of glucina have been the subject of careful study, with the result that these seem to have been discovered and some older methods shown to be 20 per cent. in error.[56] A further paper on the separation of glucinum, aluminium, chromium, and iron should help to make future determinations of glucinum easier and more accurate.[57]

[52] G. L. Heath, *J. Ind. Eng. Chem.*, 1912, **4**, 402; *A.*, ii, 1091.

[53] C. R. Sanger and O. F. Black, *J. Soc. Chem. Ind.*, 1907, **26**, 1115; *A.*, 1908, ii, 64.

[54] W. S. Allen and R. M. Palmer, *8th Intern. Cong. Appl. Chem.*, **1**, 9.

[55] B. Bleyer and A. Moormann, *Zeitsch. anal. Chem.*, 1912, **50**, 360; *A.*, ii, 491.

[56] B. Bleyer and K. Boshart, *ibid.*, 1912, **51**, 748; *A.*, ii, 1211.

[57] M. Wunder and T. Wenger, *ibid.*, 479; *A.*, ii, 687.

The difficulties which attend the estimation of chromium in chrom-vanadium steel are admirably summarised in the opening paragraph of a short paper, which proceeds to describe a good method based on the fact previously established by the author in his work on vanadium,[58] that chromium can be precipitated completely by boiling the nearly neutralised (ferrous) solution with barium carbonate, and on the observation of Noyes and Bray[59] that chromate may be separated from vanadate by precipitation as lead chromate if certain precautions are observed.[60]

Ferrous salts may be oxidised to ferric by iodine, provided the reverse reaction be inhibited by suppressing the ferric ion in the solution as it is formed, and a method based on this fact, although lacking the accuracy of the permanganate method, should prove useful because it is available in cases where organic matter and ferric salts are simultaneously present.[61] The separation of iron from titanium by volatilisation of the former as chloride may be accomplished at a lower temperature, and with simpler apparatus by substituting a carefully regulated stream of sulphur monochloride vapour for the chlorine usually employed.[62] Nitrosophenylhydroxylamine ("cupferron"), as a precipitant of copper and iron,[63] has met with comparatively little use, probably on account of its cost and of the excellent methods already available for the determination of copper and iron. In special cases, however, it has proved useful, notably as a means of separating iron from phosphates, for example in plant ashes, as a preliminary to a colorimetric determination of the iron, with which phosphates interfere.[64]

Among the usual host of papers dealing with the non-metallic constituents of steel and steel-making alloys, three call for notice. It has been shown that Ledebur's method for the determination of oxygen in iron and steel may discover none when 0·1 per cent. is present, or as little as 0·07 per cent. when 0·23 per cent. is present. An exact method is described, but it depends on the use of a 14 kw. furnace.[65] In the discussion of Blount and Levy's paper on the direct combustion method for determining carbon in steel,[66] Arch-butt drew attention to the tendency of the results so obtained to

[58] *Ann. Report*, 1911, 166.

[59] A. A. Noyes and W. C. Bray, *Techn. Quart.*, 1908, **21**, 14.

[60] J. R. Cain, *J. Ind. Eng. Chem.*, 1912, **4**, 17; *A.*, ii, 692.

[61] G. Romijn, *Chem. Zeit.*, 1911, **35**, 1300; *A.*, ii, 94.

[62] F. Bourion, *Compt. rend.*, 1912, **154**, 1229; *A.*, ii, 691.

[63] *Ann. Report*, 1910, 165; also R. Fresenius, *Zeitsch. anal. Chem.*, 1911, **50**, 35; *A.*, 1911, ii, 336.

[64] F. E. Nottbohm and W. Weisswange, *Zeitsch. Nahr. Genussm.*, 1912, **23**, 514; *A.*, ii, 690.

[65] W. H. Walker and W. A. Patrick, *8th. Inter. Cong. Appl. Chem.*, 1912, **21**, 139.

[66] B. Blount and A. G. Levy, *Analyst*, 1909, **34**, 94; *A.*, 1909, ii, 346.

exceed those yielded by wet methods, and other authors have noted a like tendency.[67] The difference appears to be due to the presence in the steel of dissolved carbonaceous gases, the carbon of which is included in the values given by the direct combustion method, and almost wholly lost in the wet methods.[68] Finally, two papers on the use of the calorimetric bomb in the estimation of carbon in steel and steel-making alloys make it appear probable that this is the only method at present available for the exact determination of carbon in certain alloys, notably high-grade ferrochromes and ferrosilicons.[69]

The bismuthate method for the estimation of manganese should be so firmly established by now as to need no defence, although it continues to meet with but slighting reference in German text-books, which rank it with the lead peroxide method. However, a miscalculation by one of its critics last year has led to two new critical investigations[70] of the method, which is shown to be at least as accurate as any known method for manganese, as it is incomparably simpler than any other method with any pretence to accuracy. A useful note has been published on its application in presence of much vanadium or chromium.[71] It has been shown that some of the disadvantages of Volhard's method disappear when it is applied to solutions of manganous nitrate instead of to solutions of the sulphate.[72]

The estimation of magnesia in limestone is referred to among new electrochemical methods, of which it is a good type, whilst the estimation of potassium hydroxide in fertilisers, soils, and plant ashes is the subject of extended notice among agricultural methods. A spectroscopic method for the estimation of small quantities of rubidium in presence of much potassium, originally designed only to determine the order of magnitude of the rubidium percentage, has proved to be accurate to ± 10 per cent.[73]

The exact determination of platinum and the preservation of platinum apparatus are intimately related problems. As the former interests comparatively few, a critical paper on the analysis of platinum ores,[74] and another on the estimation of small amounts

[67] H. Isham, *J. Ind. Eng. Chem.*, 1911, **3**, 577 ; *A.*, ii, 387.

[68] A. G. Levy, *Analyst*, 1912, **37**, 392 ; *A.*, ii, 995.

[69] P. Mahler and E. Goutal, *Compt. rend.*, 1911, **153**, 549 ; *A.*, 1911, ii, 937 ; *ibid.*, 1912, **154**, 1702 ; *A.*, ii, 807.

[70] W. Blum, *J. Amer. Chem. Soc.*, 1912, **34**, 1379 ; *A.*, ii, 1214 ; also *8th Inter. Cong. Appl. Chem.*, 1912, **1**, 61 ; H. F. V. Little, *Analyst*, 1912, **37**, 554.

[71] D. J. Demorest, *J. Ind. Eng. Chem.*, 1912, **4**, 19 ; *A.*, ii, 690.

[72] L. Karaoglanoff, *Jahrbuch Univ. Sofia*, 1910–11 ; *A.*, ii, 1214.

[73] E. Wilke-Dörfurt, *Zeitsch. anorg. Chem.*, 1912, **75**, 132 ; *A.*, ii, 686.

[74] E. V. Koukline, *Rev. Mét.*, 1912, **9**, 815.

of platinum (and gold) in silver bullion,[75] can receive no more than mention here. A paper on the error of the ordinary parting assay of platinum and silver by means of concentrated sulphuric acid, with a practical suggestion for reducing the error,[76] emphasises the connexion between the two problems, a circumstance which is still further brought out if this paper be read in conjunction with a more recent one on the protective action of a small quantity of sulphur when evaporating sulphuric acid in platinum vessels.[77] The recent work of Crookes on the volatility of the platinum metals [78] (or their oxides) confirms the conclusion of Mylius and Hüttner [79] that the improvement in the mechanical properties of platinum by alloying it with iridium is accompanied by the disadvantage that apparatus made from such alloys suffers greater changes of weight than purer platinum when subjected to the usual treatment of chemical platinum apparatus. For the most exact analytical work, therefore, pure platinum is still to be preferred, but for many purposes the mechanical properties of the alloy outweigh its disadvantages. This can scarcely be said of the alloy of rhodium with platinum. For fifty years Crookes has made the subject of the preservation of platinum apparatus so specially his own that his recommendation of rhodium alloys [80] must carry weight; but against it must be set the very careful investigation at the Reichsanstalt of a crucible which showed abnormal loss of weight each time it was heated, a property which the investigation appears to correlate with an abnormally high, although absolutely small, percentage of rhodium.[81]

As long ago as 1899 Kaufmann showed that thorium could be precipitated quantitatively, even from very dilute and strongly acid solutions, by sodium hypophosphate. It has since been found that this reaction may be used for the determination of thorium in monazite sand, an operation which it greatly simplifies.[82] So far it has received little application, and this is in part explained by the fact that the reagent is not yet procurable commercially. It is said that this difficulty will shortly be removed, but meanwhile it may

[75] F. P. Dewey, *J. Ind. Eng. Chem.*, 1912, **4**, 257; also *Chem. News*, 1912, **106**, 8; *A.*, ii, 810.

[76] A. Steinmann, *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 441, 453; *A.*, 1911, ii, 1035.

[77] L. W. McCay, *8th. Inter. Cong. Appl. Chem.*, 1912, **1**, 351.

[78] Sir W. Crookes, *Proc. Roy. Soc.*, 1912, A, **86**, 461; *A.*, ii, 563.

[79] F. Mylius and C. Hüttner, *Tätigkeitsber. d. Physik.-Tech. Reichsanstalt*; *Zeitsch. Electrochem.*, 1911, **17**, 38.

[80] *Ann. Report*, 1908, 195.

[81] Mylius and Hüttner, *loc. cit.*

[82] A. Rosenheim, *Chem. Zeit.*, 1912, **36**, 821; *A.*, ii, 869; F. Wirth, *Zeitsch. angew. Chem.*, 1912, **25**, 1678; *A.*, ii, 948.

not be amiss to call attention to a paper which gives references to the methods available for its preparation.[83]

Last year an accurate method was recorded for the determination of vanadium in the presence of chromium, but that method depended on the use of electrolytic appliances which are not available in every laboratory.[84] Another exact method, available in presence of chromium, nickel, titanium, manganese, and molybdenum, and depending on the quantitative inclusion of vanadium by the phosphomolybdate precipitate, has since been described.[85] A new method for vanadium in presence of ten times its weight of chromium appears to be exact if applied with close attention to detail,[86] but how close that attention needs to be is brought out in a joint paper by its author and J. R. Cain.[87]

In 1909, Weiss and Landecker described a number of new reactions of tantalum and columbium, and on two of them founded a new method for the separation of these two elements from titanium and from each other.[88] Their test numbers showed the method to be more accurate than other more complicated ones. It was clear from their paper, however, that success was dependent on the use of not too large a quantity of nitre in a fusion which was one step of the process, and one English abstract laid stress on this fact, and pointed out that the authors did not define this quantity with the exactness which might have been expected. With this exception the paper was so convincing that it was with surprise that the writer read last year that two other authors had investigated the method and found it wholly untrustworthy.[89] It has now been re-investigated with the result that the precipitation by carbon dioxide proposed by Weiss and Landecker is shown to be a colloid-chemical phenomenon, a fact which explains the influence of more than traces of nitrate and the results of the American critics of the method, and at the same time makes it possible to define the requisite conditions for obtaining accurate results.[90] Satisfactory results are obtained when the nitrate is omitted altogether.

A recent paper on the volumetric estimation of titanium is worthy of note, but it contains no reference to the very careful work of Gemmell,[91] which left little to be desired save increased speed. This

[83] M. Koss, *Chem. Zeit.*, 1912, **36**, 686; *A.*, ii, 809.

[84] *Ann. Report*, 1911, 165.

[85] J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, 1912, **4**, 250; *A.*, ii, 1101.

[86] D. J. Demorest, *ibid.*, 249; *A.*, ii, 1100.

[87] J. R. Cain and D. J. Demorest, *ibid.*, 256; *A.*, ii, 1101.

[88] *Ann. Report*, 1909, 147.

[89] H. W. Foote and R. W. Langley, *Amer. J. Sci.*, 1910, [iv], **30**, 401; *A.*, 1911, ii, 72.

[90] O. Hauser and A. Lewite, *Zeitsch. angew. Chem.*, 1912, **25**, 100; *A.*, ii, 262.

[91] *Ann. Report*, 1910, 168.

the latest contribution to the subject accomplishes.[92] For the estimation of very small quantities of titanium, a colorimetric method depending on the use of thymol in concentrated sulphuric acid solution has been proposed. The depth of colour produced is strictly proportional to the amount of titanium present and twenty-five times as intense as the colour produced by hydrogen peroxide.[93] As it has been shown that all phenols, especially polyhydric phenols with adjacent hydroxy-groups, give a similar reaction with quadrivalent titanium, it may be that a reagent even more sensitive than thymol might be selected.[94]

Electrochemical Analysis.

The perpetual rise in the price of platinum in part informs two other paragraphs in this report. In no branch is it more felt than in electrochemical analysis, and a paper on practical electro-analysis with the weight of the platinum apparatus reduced to 1 gram, which might some years ago have been passed by as a freak, must be regarded as a serious and valuable contribution to-day.[95] Further evidence of the utility of the mercury cathode,[96] and of the groundlessness of the objections that have been raised to it, is adduced, and it is shown that for ordinary purposes it is unnecessary to provide for the determination of the cathode potential.[97] In other respects, too, this paper is inspired by the spirit of reaction against unnecessary complexity of apparatus which was discernible in several directions last year. When a solution of iron and manganese in ammonium oxalate is electrolysed in the presence of hydrazine sulphate, iron is deposited quantitatively, whilst the hydrazine prevents the deposition of manganese dioxide at the anode.[98] Copper, tin, antimony, and bismuth can be deposited quantitatively and fairly quickly from hydrochloric acid solutions, provided a reducing agent, such as hydroxylamine hydrochloride, is present.[99] The electrolytic estimation of zinc in presence of ammonium salts must take place in acid solution, and has been possible hitherto only when rotating electrodes are employed. It is now found that stationary electrodes may be employed provided that lactic acid and an alkali lactate are present.[1]

[92] P. W. and E. B. Shimer, *8th. Inter. Cong. Appl. Chem.*, 1912, **1**, 445.
[93] V. Lenher and W. G. Crawford, *ibid.*, 285.
[94] O. Hauser and A. Lewite, *Ber.*, 1912, **45**, 2480; *A.*, i, 847.
[95] F. A. Gooch and W. L. Burdick, *Zeitsch. anorg. Chem.*, 1912, **78**, 213; *Amer. J. Sci.*, 1912, [iv], **34**, 107; *A.*, ii, 986.
[96] *Ann. Report*, 1910, 170; *ibid.*, 1911, 168.
[97] P. Baumann, *Zeitsch. anorg. Chem.*, 1912, **74**, 315; *A.*, ii, 489.
[98] R. Belasio, *Ann. Lab. Gabelle*, 1912, **6**, 207; *A.*, ii, 1097.
[99] E. P. Schoch and D. J. Brown, *8th Inter. Cong. Appl. Chem.*, 1912, **21**, 81.
[1] R. Belasio, *Ann. Lab. Gabelle*, 1912, **6**, 239; *A.*, ii, 1096.

An interesting example of another type of electro-analytical method is one which seeks to determine magnesium in presence of calcium by titration of the magnesium, making use of the fact that when alkali hydroxide is added to a neutral solution containing salts of calcium and magnesium the concentration of hydroxyl ions increases very slowly until all the magnesium is precipitated as hydroxide and then increases rapidly to the point at which calcium hydroxide begins to separate.[2] A somewhat similar method applied to an easier problem is that which determines nitric acid in a mixture of sulphuric and nitric acids by neutralising the solution with barium hydroxide, and then titrating it with sodium carbonate until the sharp rise in the conductivity announces the complete precipitation of the barium.[3] Applied to mixtures of sulphuric and nitric acids containing only traces of other substances, the method gives accurate results, but the method of Dutoit and Duboux, for the determination of sulphates in wine,[4] which suggested it, has now been shown to be untrustworthy. The results of Dutoit and Duboux are not impeached, but their accuracy is shown to be quite fortuitous.[5] On the other hand, it has been shown that calculation of the sulphate in water from the known chloride and nitrate content and the conductivity, whatever objection may be raised to it, is capable of yielding fair results.[6]

Organic Analysis.

Three papers on qualitative methods may be mentioned, namely, one in which the colour developed on treatment with potassium dichromate and sulphuric or nitric acid is used to divide amino-compounds into four main groups,[7] one which provides a system for distinguishing a number of the simpler phenols,[8] and one which serves for the detection of small quantities of maltose, lactose, and melibiose when these occur together.[9]

Early this year Hibbert issued a warning that the method devised by himself and Sudborough for the estimation of hydroxy-, amino-, and imino-derivatives by means of Grignard's reagent,[10] was not so generally applicable as had been supposed,[11] but it has

[2] J. H. Hildebrand and H. S. Harned, *8th Inter. Cong. Appl. Chem.*, 1912, **1**, 217.
[3] H. Corvazier, *Mon. Sci.*, 1912, [v], **2**, I, 322 ; *A.*, ii, 1092.
[4] *Ann. Report*, 1908, 207.
[5] A. Bruno and P. T. D'Auzay, *Compt. rend.*, 1912, **154**, 984 ; *A.*, ii, 600 ; *Ann. Chim. anal.*, 1912, **17**, 243.
[6] F. Dienert, *ibid.*, 1701 ; *A.*, ii, 807.
[7] H. Agulhon and P. Thomas, *Bull. Soc. chim.*, 1912, [iv], **11**, 69 ; *A.*, ii, 308.
[8] J. A. Sanchez, *ibid.*, 1911, [iv], **9**, 1056 ; *A.*, ii, 209.
[9] C. Neuberg and S. Saneyoshi, *Zeitsch. Ver. deut. Zuckerind*, 1912, 559.
[10] *Ann. Report*, 1911, 170. [11] H. Hibbert, *T.*, 1912, **101**, 328.

since been shown that Zerewitinoff's modification, using pyridine as solvent, gives theoretical results with each of the substances which behaved anomalously in Hibbert's hands. The method has now been extended to diamines of the aliphatic, benzene, diphenyl, stilbene, and naphthalene series, and it is found that such substances react with two atoms of "active hydrogen" at room temperature, and with three atoms at 85°, but that the fourth atom does not react at all with magnesium methyl iodide. The one exception so far recorded is malonamide, which reacts with four atoms. The hydrocarbons of the indene and fluorene type do not react at the ordinary temperature, but at 85° a quantity of methane is obtained corresponding with one atom of "active hydrogen."[12]

This report provides an opportunity for calling attention to a method for the determination of benzaldehyde, which might otherwise escape attention, owing to its inclusion in a paper with a more general title. It depends on the use of *p*-nitrophenylhydrazine, and is shown to be far more accurate than any other available method. The same method yields even better results with anisaldehyde and vanillin, but these aldehydes can be determined with equal accuracy by other means.[13] A new colorimetric method for the estimation of vanillin, simpler than the methods usually employed, is shown to give accurate results when applied to genuine extracts,[14] but since it depends on the use of a reagent which yields a similar colour with all substances containing phenol groups,[15] it cannot be applied to extracts of unknown origin. The estimation of furfuraldehyde is of importance in the estimation of pentoses and pentosans, and the description of a new method,[16] which avoided the use of phloroglucinol and promised to be more expeditious than the phloroglucinol method, was welcome. It depends on the reduction by furfuraldehyde of Fehling's solution, but its author erred in supposing that the ratio of furfuraldehyde to copper reduced was independent of the concentration. However, the reducing power over a range of concentrations covering those which occur in practice has since been determined, and the method at the same time simplified.[17]

König and Hühn, having applied each of the principal methods for the determination of cellulose in woods and textile fibres to a number of typical raw materials, reach the conclusion that

[12] T. Zerewitinoff, *Ber.*, 1912, **45**, 2384; *A.*, i, 841.
[13] B. G. Feinberg, *8th Inter. Cong. Appl. Chem.*, 1912, **1**, 187.
[14] O. Folin and W. Denis, *J. Ind. Eng. Chem.*, 1912, **4**, 670.
[15] O. Folin and W. Denis, *J. Biol. Chem.*, 1912, **12**, 239; *A.*, ii, 1011
[16] J. T Flohil, *Chem. Weekblad*, 1910, **7**, 1057; *A.*, 1911, ii, 160.
[17] L. Eynon and J. H. Lane, *Analyst*, 1912, **37**, 41; *A.*, ii, 305.

König's method,[18] in spite of the low yield of cellulose obtained, is the best one for the quantitative determination of that constituent. Next to König's, the method of Tollens-Dmochowski[19] is preferred, according to which hydrolysis by the Weende-Henneberg ("crude fibre") process is followed by oxidation with nitric acid. It is said that Cross and Bevan's chlorination method fails to remove most of the hemi-hexosans and pentosans.[20] Cross and Bevan remain convinced that the chlorination process, properly controlled, will remain the standard method for the estimation of cellulose.[21] Where experts differ so widely, it is not for the present writer to express an opinion, but it is permissible to say that the issue seems to turn on the definition of "cellulose."

Innumerable methods have been described for the detection and approximate estimation of small quantities of methyl alcohol. For some of these, based on the oxidation of the methyl alcohol to formaldehyde and detection of the latter by some old or new reagent, an extraordinary degree of sensitiveness has been claimed. In practice, however, most of them have proved to be at the most but new colour reactions of formaldehyde, for which other tests of great delicacy have long been known, whilst they did nothing to advance the practical problem of detecting methyl alcohol in the presence of ethyl alcohol, since, unless the oxidation is carefully regulated, ethyl alcohol gives rise to acetaldehyde, which interferes with some of the tests, or even to formaldehyde, which upsets them all. As a result of a careful study of the conditions necessary to preserve the ethyl alcohol from oxidation, one of the later proposals of Denigès[22] has been so far improved upon that it is now possible to detect with certainty 0·05 per cent. of methyl alcohol in 90 per cent. alcohol, and to determine larger quantities with an error not exceeding 4 per cent. of the amount of methyl alcohol present.[23] A novel proposal for the estimation of alcohol in pure aqueous solution depends on the fact that when sufficient potassium fluoride is added to such solutions, two phases separate. If water be now added gradually, a point is reached when the solution again becomes homogeneous, and this point can be determined very closely if a little solid spirit blue is present, since this makes a very thin film of alcohol easily visible. The paper is accompanied by tables for

[18] J. König, *Ber.*, 1908, **41**, 46 ; 1908, ii, 236.

[19] R. Dmochowski and B. Tollens, *J. Landw.* 1910, **58**, 1 ; *A.*, 1910, ii, 554.

[20] J. König and F. Hühn, *Zeitsch. Farb. Ind.*, 1911, **10**, 297, 236, 344, 366 ; 19 **2**, **11**, 4, 17, 37, 57, 77, 102 ; *A.*, ii, 1005.

[21] C. F. Cross and E. J. Bevan, *ibid.*, 1912, **11**, 197 ; *A.*, ii, 1105 ; also *8th Inter. Cong. Appl. Chem.*, 1912, **13**, 101.

[22] G. Denigès, *Compt. rend.*, 1910, **150**, 832 ; *A.*, 1910, ii, 461.

[23] C. Simmonds, *Analyst*, 1912, **37**, 16 ; *A.*, ii, 208.

the use of the analyst. Although potassium fluoride cannot be used for the production of alcohol of a strength exceeding 97·5 per cent., its dehydrating action is more rapid than that of most drying agents, and it absorbs as much as 62 per cent. of its weight of water against 32 per cent. taken up by lime.[24]

An interesting development of Walden's observation that, under certain conditions, uranyl salts produce a marked change in the specific rotation of *l*-malic acid, is a practical method for the estimation of malic acid in fruit juices.[25] The determination of small quantities of salicylic acid in presence of much *p*-hydroxybenzoic acid is less frequently required than the converse proposition, but a method by which it may be effected is interesting as an example of a new type of biochemical method of analysis. It depends on the fact that *Penicillium glaucum* can utilise *p*-(and also *m*-)hydroxybenzoic acid for its nutrition, whilst salicylic acid, in quantities of more than 1 per cent., greatly retards, if it does not wholly inhibit, the growth of the organism.[26]

Attention may be directed to two papers on the volumetric estimation of azo-dyestuffs by means of hyposulphite. If the limitations of the method are obvious, so are its practical advantages in cases where the results of the titration are free from ambiguity.[27]

The selection, for notice in this report, of methods relating to the analysis of foods, drugs other than definite chemical substances, and still more of natural fats and oils, is attended with difficulty. Of the papers that one can point to as unquestionably of value, the majority concern themselves with constants and ratios, and although in the aggregate they advance our knowledge considerably, it is only occasionally that any one or any group carries our knowledge of some problem of general interest to a point where a summary of progress made can be usefully attempted. Of new methods experience forbids one to expect that more than a very few will prove at the best more than alternatives for existing ones, whilst by nothing short of actual trial can one distinguish between tests like that of Halphen for cottonseed oil, which has proved specific and approximately quantitative, and the hundreds of colour tests which have been described since, and since forgotten. Even Halphen and those who have used his test for fifteen years have

[24] G. B. Frankforter and F. C. Frary, *8th Inter. Cong. Appl. Chem.*, 1912, **22**, 87.

[25] P. B. Dunbar and R. F. Bacon, *J. Ind. Eng. Chem.*, 1911, **3**, 826; *A.*, ii, 699.

[26] J. Böeseken and H. J. Waterman, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 604; *A.*, ii, 306.

[27] E. Grandmougin and E. Havas, *Chem. Zeit.*, 1912 **36**, 1167; *A.*, ii, 1220; W. Siegmund, *Monatsh.*, 1912, **33**, 1431; *A.*, 1913, ii, 82.

been lucky if the recent statement proves correct that Halphen's reaction fails if the amyl alcohol employed is a carefully purified sample.[28] Fortunately, even if true, this does not touch the principle of Halphen's test, as Veley's work did absolutely destroy the whole basis of the Girard-Cuniasse method for the determination of the higher alcohols in potable spirits, and as Chapman's work limited the conclusions to be drawn from the so-called tests for creatinine and hydrogen cyanide by means of picric acid. The history of these three methods, however, one good, one bad, and one indifferently good, but all at some time in daily use by many food analysts, goes to show that the early literature of a colour reaction is not likely to provide internal evidence by which it may be appraised.

It was stated by the reporter of 1910, whose opinion on this subject is entitled to special respect, that the methods of Jolles and Lemeland for the estimation of sucrose in presence of reducing sugars, even if trustworthy, which was open to doubt, had no advantage over existing methods.[29] That neither is as accurate as might be desired has since been demonstrated, but the former is shown to afford a ready means of determining sucrose in condensed milk with a satisfactory degree of accuracy,[30] whilst the latter has been so far improved that, in its modified form, it is recommended as a substitute for the Clerget-Herzfeld inversion method in the analysis of sugars and syrups, and especially as a routine method for the determination of the sucrose-content of low-grade products like hot-room goods.[31]

Reference was made last year to a cryoscopic method for determining whether a sample of milk, abnormally low in non-fatty solids, owed its abnormality to addition of water or to natural causes.[32] For three years the method has been applied to all doubtful samples in the Government Laboratory at Brisbane,[33] but unfortunately it seems to form no part of the duty of any official in this country to investigate a method a knowledge of which might perhaps have reduced the number of cases of miscarriage of justice in the autumn of 1911. Richmond's annual paper on the composition of milk shows that the average for non-fatty solids fell in August, 1911, almost to the legal minimum, whilst 27 per cent. of all the samples examined were below the standard.[34] In only a

[28] E. Gastaldi, *Ann. Lab. Gabelle*, 1912, **6**, 601; *A.*, ii, 1108.
[29] *Ann. Report*, 1910, 174.
[30] H. Nowak, *Zeitsch. anal. Chem.*, 1912, **51**, 610; *A.*, ii, 1004.
[31] W. E. Cross and W. G. Taggart, *Intern. Sugar J.*, 1912, **14**, 444.
[32] *Ann. Report*, 1911, 173.
[33] J. B. Henderson, *Aus. Assoc. Adv. Sci.*, 1912, 13.
[34] H. D. Richmond, *Analyst*, 1912, **37**, 298.

few cases, however, was evidence of this kind available at the time, and in not all of those cases did it carry the necessary weight because based on comparatively few samples.

Fiehe and Stegmüller have examined most of the methods which have been proposed for the examination of honey, and give detailed directions for carrying out the tests they have found most useful.[35] Fiehe's test for artificial invert sugar[36] is now firmly established, but has perhaps not reached its final form, as another new reagent has been recommended,[37] whilst useful suggestions have been made for avoiding the interference of formaldehyde and some other substances which may be present,[38] and a third paper gives hints on precautions to be observed in carrying out the process, some of which may save the analyst trouble.[39] Langer's serological test[40] has been further studied, and it is found that the quantity of the precipitate is not diminished by previously heating the honey unless a temperature approaching 100° is reached, and maintained for ten minutes or longer.[41]

A new method for the estimation of shell in cocoa powders depends on the precipitation of cocoa-red by means of ferric chloride from an acetic acid extract of the cocoa. It is claimed that it will detect with certainty the addition of 10 per cent. of shell to "normal cocoa." In conjunction with other tests, it may prove useful, but the figures given in the paper show that, if this test were the sole criterion, it would be possible to add nearly 40 per cent. of shell to cocoa from one part of the world, and then plead as excuse, for its low content of cocoa-red, the normal content of the latter in cocoa grown elsewhere.[42] T. Macara has developed Filsinger's levigation method for the determination of shell to such an extent that the authors of a recent book,[43] as yet the only place of publication of the modified method, express the opinion that it is of more value than any chemical method yet available for the purpose. Another mechanical method depends on the use of a mixture of chloral hydrate, glycerol and water, having a specific gravity of 1·5, and the use of a centrifuge to separate the heavier portions of the shell (about a third of the whole) from the rest of the mixture.[44]

[35] *Arbeit. Kaiserl. Gesundheitsamte*, 1912, **40**, 305.
[36] *Ann. Report*, 1910, 174; 1911, 174.
[37] G. Armani and J. Bartoni, *Ann. Lab. Gabelle*, 1912, **6**, 85.
[38] G. Halphen, *Ann. Falsif.*, 1912, **5**, 105; *A.*, ii, 498.
[39] L. Stoecklin, *ibid.*, 116; *A.*, ii, 499.
[40] *Ann. Report*, 1910, 174; 1911, 174.
[41] J. Thöni, *Mitt. Lebensmitteluntersuch. u. Hyg.*, 1912, **3**, 74; *Chem. Zeit.*, 1912, II, 151.
[42] C. Ulrich, *Arch. Pharm.*, 1911, **249**, 524.
[43] "Fatty Foods," by E. R. Bolton and C. Revis (Churchill), 303.
[44] L. Kalusky, *Zeitsch. Nahr. Genussm.*, 1912, **23**, 654.

Concerning the best method for the determination of nicotine in tobacco extracts, there is still disagreement, but the method of Bertrand and Javillier,[45] depending on the precipitation of nicotine by means of silicotungstic acid, is now admitted by Tóth—the author of a rival method—to leave nothing to be desired in point of accuracy.[46] Thus at least three methods have survived the criticism which has been so active during the last three years.[47] There can be no doubt, however, that that criticism has sounded the death-knell of the method of Ulex after a useful life of twenty-five years, although there are commercial reasons for believing that its burial may be deferred.[48]

Attention may be directed to a new method for the separate determination of citronellal and geraniol in citronella oil,[49] and to another for the direct determination of the geraniol, which depends on the conversion of the citronellal into its oxime, which passes into the nitrile on boiling with acetic anhydride to acetylate the geraniol, the nitrile being unaffected by the potassium hydroxide subsequently used to saponify the acetylated oil.[50]

A recent method for the determination of the preservative, soft resins, in hops is probably the most accurate yet described. That it will prove too tedious for commercial purposes is recognised by its authors, but they have made use of it to compare the accuracy of the quicker methods in general use.[51] They find that the latest form[52] of Lintner's volumetric method gives results within a few tenths of 1 per cent. of those yielded by their own, whilst that of Briant and Meacham,[53] the first practical method evolved for the purpose, and still the prevailing one in this country, always underestimates the soft resins, and may in some cases underestimate them by as much as 50 per cent. The paper is written with a clearer appreciation of earlier work than is usually shown by writers on this subject, the literature of which is difficult to piece together.

Mention is made earlier in this report of the use of the calorimetric bomb in the determination of carbon in steel. A similar method is now employed in the United States Bureau of Mines

[45] G. Bertrand and M. Javillier, *Bull. Soc. chim.*, 1909, [iv], **5**, 241; *A.*, 1909, ii, 450; *Ann. Chim. anal.*, 1911, **16**, 251; *A.*, 1911, ii, 827.

[46] J. Tóth, *Chem. Zeit.*, 1912, **36**, 937; *A.*, ii, 1010.

[47] *Ann. Report*, 1911, 174.

[48] See, for instance, F. Porchet and P. Tonduz, *Chem. Zeit.*, 1912, **36**, 843; R. Kissling, *ibid.*, 1321.

[49] V. Boulez, *Bull. Soc. chim.*, 1912, [iv], **11**, 915; *A.*, ii, 1105.

[50] J. Dupont and L. Labaune, *Ann. Chim. anal.*, 1912, **17**, 210; *A.*, ii, 697.

[51] H. V. Tartar and C. E. Bradley, *J. Ind. Eng. Chem.*, 1912, **4**, 209.

[52] C. J. Lintner, *Chem. Zeit.*, 1908, **32**, 1068; see also D. Neumann, *Wochensch. f. Brauerei*, 1910, **27**, 281.

[53] L. Briant and C. S. Meacham, *J. Inst. Brewing*, 1897, **3**, 233.

for the determination of sulphur in oils and all other combustible materials. The method is rapid and as accurate as any. Of the other methods available for this determination in oils, only that of Carius and those depending on combustion in a current of oxygen are accurate. None of the methods depending on combustion in oxygen contained in a large glass bottle is trustworthy, nor are methods depending on fusion with alkalis and subsequent oxidation, fusion with alkalis and an oxidising agent, or wet treatment with alkalis and oxidising agents, although the three last types of method, of which there are many varieties, are excellent for solid fuels.[54] Ten methods, all of which find use for the determination of water in petroleum, have been subjected to a critical examination, and it is found that the most accurate is that depending on the volume of hydrogen evolved when the sample is treated with finely-cut sodium.[55]

Agricultural Analysis.

Subject to correction by those exclusively devoted to agricultural chemistry, the writer would characterise as the most important paper affecting British agricultural analysts, one on the estimation of potassium.[56] Yet there is little in the paper that is new. It is shown that the perchlorate method is far superior to the platinum method, not only on the ground of cost, but as being freer from error, simpler, and less likely to give rise to differences between different analysts. All this information was available at least as long ago as 1909, when Precht stated that the perchlorate method had almost superseded the platinum method throughout Germany.[57] The present paper includes an improvement on Neubauer's simplified method, which will prove of special value in dealing with small quantities of precipitate, but the importance of the paper as a whole depends less on the new information it conveys than on the fact that it is dated from Rothamsted, and may therefore expect to result in action by the Board of Agriculture, which apparently is not advised of analytical progress in foreign countries. The case is urgent. Analysts under the Fertilisers and Feeding Stuffs Act are required to determine potassium in fertilisers by the platinum method, to take large quantities of substance for analysis, and to make declaration that the analysis was made in accordance with these and other directions of the Board,[58] and these regulations neces-

[54] I. C. Allen and I. W. Robertson, *8th Inter. Cong. Appl. Chem.*, 1912, **10**, 25.

[55] I. C. Allen and W. A. Jacobs, *ibid.*, 17.

[56] W. A. Davis, *J. Agric. Sci.*, 1912, **5**, 52.

[57] Precht, *7th Inter. Cong. Appl. Chem.*, 1909, **1**, 146 ; also *6th Congress*, 1906.

[58] Board of Agriculture and Fisheries, *Statutory Rules and Orders*, 1908, No. 964.

sarily affect the practice of other analysts besides official agricultural chemists. If the platinum method is to be used, the use of large quantities makes for accuracy, yet quite recently two of the best known London analysts differed by nearly 3 per cent. in the case of a sample of 90 per cent. sulphate of potash.[59] In view of facts such as these, there is no necessity or excuse for deferring the official dethronement of the platinum method until the perchlorate method, which admittedly falls short of exactness, has been further refined A notable feature of the paper is the frankness with which numbers leaving much to be desired in point of accuracy are used to sustain the argument and yet not overstate the case. Since frequent alterations of official methods of analysis are attended with inconvenience, the Board might at the same time invite private criticism of their other methods of analysis with a view to the re-casting of these. So unfortunately are they worded that the writer has heard it suggested that they must be the work of a chemist with so strong an objection to the principle of official methods that he drafted this set to discredit that principle. The writer must not be held to endorse this opinion, but that it can be expressed, even in jest, reflects seriously on a document which has the force of law.

Modern legislation has made official methods necessary, but in some cases the legislative enactments or statutory rules and orders made under them have been in advance of the knowledge necessary to frame satisfactory methods. A case in point is the use of a standard solution of ammonium citrate. Such a method has been official in the United States for some years, and the American chemists did their best to define the hydrion concentration—on which the results obtained by the use of the solution are closely dependent—so far as this could be done with chemical indicators. Yet it is possible for two chemists, experienced in the method, to report, one 3 per cent., the other 5 per cent. of insoluble phosphate in one and the same sample. If electrical appliances are available for determining the hydrion concentration of the standard solution, satisfactory concordance is easily established, but many laboratories lack the necessary equipment.[60] Fortunately, this test is not official in Great Britain, but in at least one of our colonies every fertiliser must be registered with a declaration, which must also appear on invoices, that it contains not less than so much "citrate-soluble" phosphoric acid. A proclamation by the Governor of the Colony[61] defines the strength of the citric acid solution to be used

[59] Davis, *loc. cit.*

[60] A. J. Patten and C. S. Robinson, *J. Ind. Eng. Chem.*, 1912, **4**, 443; *A.*, ii, 1094.

[61] Proclamation by the High Commissioner for South Africa, 5 Dec., 1910.

with basic slag, which is identical with that in use in nearly all civilised countries, but is silent concerning the more or less neutral solvent to be applied to all other fertilisers, which demanded rigid definition, if indeed the use of such a solution for official purposes can be recommended at all in the present state of our knowledge.

A discussion on the methods available for the rapid yet sufficiently exact determination of phosphoric acid in soils[62] was chiefly remarkable for the absence of any reference to the lead molybdate method,[63] which, if not quite so rapid as some, is probably the most exact of the approximate methods, and possibly the most exact method available where the quantity to be determined is very small.

Water Analysis.

It is on the actual concentration of hydrogen ions, and not on the potential acidity or alkalinity as given by ordinary titration, that the rate of action of water on metals depends. Electrical measurements of this concentration are difficult in some circumstances—for example, on board ship—and require appliances not at the disposal of every analyst. Modifications of Sörensen's method of colour comparison with standards prepared from the salts Na_2HPO_4 and KH_2PO_4, water and standards alike being tinted with a suitable indicator, are free from this objection, and the use of his method made possible the collection of much useful information during a cruise made for hydrographical purposes from the Baltic to the Black Sea.[64] A recent proposal to state the results of such a comparison in a new way, although certain to arouse criticism, will commend itself to the water analyst, and do much to establish the method as a recognised part of a complete water analysis. Briefly, the proposal is to state the acidity or alkalinity of a solution in terms of the acidity or alkalinity of water at the same temperature; thus a water with a hydrion concentration of $1{\cdot}36 \times 10^{-7}$ at 18° would be said to have a relative acidity of 2 or relative alkalinity of 0·5. One advantage of the method is that the results thus stated are nearly independent of temperature. Another and by no means insignificant one, is that the client without scientific knowledge will have less difficulty in appreciating the significance of the analyst's numbers. The proposal is accompanied by tables which do away with all calculation, and place the method at the disposal of anyone who will make up two standard solutions.[65]

[62] S. J. M. Auld, *Analyst*, 1912, **37**, 130.

[63] H. Brearley and F. Ibbotson, *Analysis of Steel-Works Materials* (Longmans), 55.

[64] Palitzsch, *Compt. rend. des Travaux du Lab. de Carlsberg*, 1911, **10**, 85; also *Biochem. Zeitsch.*, 1911, **37**, 116; *A.*, ii, 39.

[65] J. Walker and S. A. Kay, *J. Soc. Chem. Ind.*, 1912, **31**, 1013; *A.*, ii, 1215.

A paper which draws attention to the fact that, in carbonated waters, ammonia may be much underestimated, unless special precautions be taken, should not be overlooked, although other methods for securing accurate results, besides that proposed by the authors, may readily suggest themselves.[66] Since the last reference to water analysis in these reports,[67] Chamot and Pratt, in collaboration with Redfield, have brought to a conclusion their important researches in connexion with the estimation of nitrates by the Grandval and Lajoux method. Those researches have laid bare the mechanism of the Grandval and Lajoux reaction, hitherto wholly misconceived, and establish on sound principles the precautions necessary to attain the best results of which the method is capable, but these precautions and the results are such that the authors may be said to have assisted to destroy the method to the investigation of which they have given so much labour. To known waters the method may often be applied, and in such cases reference to the work cited will save the analyst trouble and increase the accuracy of his results; but as a general method it cannot compare with others which are nearly if not quite as quick and far more trustworthy.[68]

G. Cecil Jones.

[66] G. D. Elsdon and N. Evers, *Analyst*, 1912, **37**, 173; *A.*, ii, 601.

[67] *Ann. Report*, 1910, 181.

[68] E. M. Chamot, D. S. Pratt, and H. W. Redfield, *J. Amer. Chem. Soc.*, 1911, **33**, 366, 381; *A.*, 1911 ii, 331.

PHYSIOLOGICAL CHEMISTRY.

During the year 1912 no prominent person in the bio-chemical world has passed away, nor are there any new books in this branch of science to announce. The only item of general news necessary to mention is the fulfilment of the hope expressed in last year's report that the Bio-chemical Club founded in 1911 would blossom into a Society with a journal of its own. This is now an accomplished fact. The *Bio-chemical Journal*, which has hitherto been edited by Professor Benjamin Moore and Mr. Whitley, of Liverpool, will in future be conducted by the newly-founded Bio-chemical Society, and issued by the Cambridge University Press. As editors, the services of Professor W. M. Bayliss and Dr. A. Harden have been secured; bio-chemists will watch with interest the new enterprise, and wish it every success.

Periodical literature, which it is the special duty of this report to review, was never more bulky; physiological chemistry is still remarkable among the sciences for its fruitful and steady growth. The papers published deal with every corner of the science, and add fresh bits of knowledge to many subjects. The mere fact, however, that in the general run the expression "bits of knowledge" is correct, renders the arrangement of a systematic résumé difficult within a reasonable space.

Among the many problems at which work has been diligently directed the following few are the most important. The gaseous metabolism in individual organs is still steadily being examined under the leadership of J. Barcroft, but there are no striking new facts. What has appeared relates to organs other than those previously examined, the same methods with slight modifications here and there having been employed. This sort of work is none the less valuable, but the accumulation of data is always dull work from the reviewer's point of view. Closely allied to this question is the continued discussion as to whether there are any circumstances under which the lining membrane of the lung actively secretes oxygen into the blood. J. S. Haldane and his co-workers have definitely abandoned the view that such secretion takes

place normally, and investigators are now happily unanimous that physical diffusion alone explains the gaseous interchanges which occur in the lung. The upholders of the secretion theory, however, still feel doubt whether that theory should be abandoned altogether, and believe that under stress (for instance, at great altitudes) the pulmonary epithelium is able to exercise the property of piling up oxygen into the blood which it inherits from the swim-bladder of the fish. Renewed work can alone show whether they are right.

The ductless glands are still fertile fields for work, and perhaps the most interesting papers which have appeared on this subject are those by Prof. Carlson and his colleagues at Chicago on the relationship of the thyroid and parathyroid bodies to tetany. The action of adrenaline again is not fully worked out yet, and quite a large number of papers have appeared on this subject.

One only I will mention a little more fully in passing. It is often noticed that the effect of a drug on an isolated organ differs from that which ensues when the same organ is in the intact body: for a drug may act indirectly on an organ by stimulating the suprarenal gland to activity, and the effect observed is really an adrenaline effect. Dale and Laidlaw [1] have worked out this question especially on the uterus and on the eye, and it appears likely that this factor will play an important part in future investigations; and no doubt other organs than the suprarenal will have also to be reckoned with.

Since the foregoing paragraph was written, a series of papers [2] from Starling's laboratory has appeared, which demonstrate the importance of the suprarenal factor in many cases of elevated blood-pressure where it was previously unsuspected. The rise of arterial pressure which occurs, for instance, when the splanchnic and other nerves are irritated, or when the amount of carbon dioxide in the blood is increased, is in part due to the pouring out of adrenaline into the circulation.

The activities of enzymes of all sorts, the lipoids, creatine and creatinine, the scientific exploration of drug actions, the large subject of immunity and its offshoots, such as anaphylaxis, all these and many others claim mention in the year's output.

The wide word metabolism covers a multitude of researches, and nearly every aspect of this important subject has received attention. One may particularly single out, for a passing reference, the question of nuclein metabolism, and express the hope that Levene

[1] *Proc. physiol. Soc.*, 1912, xii, *J. Physiol*, **44** *A.*, ii, 667. Also *J. Physiol*, 1912, **45**, 1; *A.*, ii, 854.

[2] G. von Anrep, *J. Physiol*, 1912, 307, 318; S. Itami, *ibid.*, 338; *A.*, 1913, i, 121, 136.

and his fellow-workers will succeed in unravelling the constitution of the animal nucleic acids. I dealt with the question of nucleic acid at some length last year, and it is too soon to make fresh pronouncements; the nucleic acid which Levene made the subject of his noteworthy work was mainly of vegetable origin (for instance, that of yeast), and this he showed to be a complex of phosphoric acid, certain bases, and a pentose (ribose). In the acid of animal origin (for instance, that from the thymus gland), the place of the pentose is taken by a hexose, and one awaits with considerable interest the work already started in relation to it.[3]

After this rapid review of some of the aspects of the year's work, let us now pass on to enumerate the subjects which I have chosen for a more extended notice.

I shall take up first one or two subjects suggested by the well-worn but still unsettled theme, "The origin of life." Next I propose to deal with certain aspects of metabolism, namely, repair, growth, and synthesis in the animal body. Then will follow somewhat more briefly a review of a few important recent papers on blood-clotting, and finally I shall conclude with equally short references to two pathological subjects, namely, dropsy and neuritis.

The Origin of Life.

This subject loomed large on the horizon during the autumn, for it was naturally the part of Professor Schäfer's Presidential Address at the Dundee meeting of the British Association which attracted popular attention. The extremely useful and lucid account of recent physiological progress which he gave as a sequel to the more speculative portion that opened the address passed almost unnoticed. We should all, of course, like to know for certain what was or what is the actual origin of life on this planet, but that, also of course, was just what Professor Schäfer failed to give us. The speculations advanced were given with due scientific caution, and as the years go by and knowledge grows, hypotheses rest on surer foundations, but the time has not yet arrived when one can assert with safety that a living organism or a living molecule is only the result of chemical and physical forces operating on inorganic parent material. One may perhaps be bold enough to state that it is becoming more and more difficult to deny such an assertion.

It is not, however, my object to continue in these pages the lengthy and sometimes futile discussions which sprang out of the address, in the newspapers, at the sectional meetings of the Association itself, and more recently in *Science Progress*. It however

[3] Levene and Jacobs, *J. Biol. Chem.*, 1912, **12**, 377, 411; *A.*, i, 926.

occurred to me that it might be of interest to deal with one or two rather more matter of fact pieces of original research which are suggested by the phrase "The origin of life," although the relationship may not be obvious at first sight.

The first of these may be entitled the *Continuance of Life*. From the very earliest days of scientific physiological experiment the importance of a study of the excised portions of a dead frog's body was recognised, and our fundamental notions of such phenomena as the contraction of muscles and the beating of the heart are derived from such investigations. The far-reaching results which have followed the investigation of what it is now the custom to term "surviving organs" are known to every physiologist, and are apprehended even by the first year's student of that science. Now that it is possible to apply this method to mammalian organs also, the additions to knowledge have been still greater and of more practical benefit. Thanks to the fluid known as Ringer's solution as modified by Locke, one is now able to keep an isolated mammalian heart under observation, and manifesting all its living activities for hours, and even for days. Thanks to Ross Harrison's microscopic technique, it is possible to keep snippets of embryos small enough for histological observation, alive and active in a hanging drop of lymph; one can see the cilia still moving, one can witness the transformation of an undifferentiated protoplasmic mass into a striated muscle fibre, and, above all, one can watch the nerve fibres growing out of nerve cells, and shooting forth in a distal direction at no mean speed. Harrison was thus able to show by direct ocular evidence the truth of His's doctrine that the peripheral nerves are the outgrowths distalwards of processes from the central nerve cells, a doctrine which was accepted previously on circumstantial evidence alone.

It is true that in such observations, no living properties are bestowed on the matter under observation, but the mere fact that living activities can be maintained by purely artificial means of a chemical nature, after the organism as a whole is dead, renders it increasingly difficult to postulate any specific and mysterious vital force.

Wonderful as such results are, they are entirely thrown into the shade by the more recent achievements of certain investigators at the Rockefeller Institute of New York. By the use of appropriate culture fluids, the cells of cancerous and other tumours have been watched growing and multiplying for weeks, and A. Carrel[4] has succeeded in keeping his tissues alive longer than two months. In general terms the culture media employed are the plasma and

[4] *J. Experim. Med.*, 1912, **15**, 516; **16**, 165.

serum of blood at a suitable temperature, but the tissues remain in a latent phase in cold Ringer's solution, and resume activity when warmed. His most striking experiment was done with fragments of heart muscle; such fragments grew and commenced to pulsate, and were still pulsating *in vitro* three months after they were removed from the body. Carrel was previously known for his expert surgical skill in transplanting blood vessels and other organs, an entirely different branch of research, and the Nobel Prize he has just been awarded is some slight recognition of the value of his investigations.

The other set of experiments to which we will now pass are in a sense the counterpart of these. Just as organs which under ordinary conditions would be dead can be made to live, so methods which were previously employed only for dead organs can now be applied to those which are alive. I refer to what is called *Intravitam staining*, of which Prof. Goldmann, of Freiburg, is the chief exponent. Prof. Goldmann has published several monographs on this subject, and his most recent one is in the *Beiträge f. Klin. Chir.*[5] A very useful summary of his main results appeared in the *Proceedings* of the Royal Society about the same date.[6] The older methods in which methylene-blue was injected into the blood stream were limited to the differentiation of specific tissues; Ribbert was the first to attempt a vital stain by intravenous injection of carmine; but the results achieved were so uncertain that such methods never passed into general use, and the toxic effects of the injections were usually sufficient to kill the animal.

A new departure in this field resulted from the attempts to cure diseases caused by trypanosomes and other protozoan parasites through the agency of aniline dyes, such as trypan-red and trypan-blue; and Bouffard, of the Pasteur Institute, investigated the histological appearances in the cells of the body which ensued. Quite independently Goldmann took up similar work, and made an extensive study of normal rats and mice injected with trypan-, isamine-, and pyrrhol-blue solutions. His early results were published in 1909, and since then his method has been improved, and the work extended to include pathological conditions. After such injections the animal suffers from no ill-effects, and the only outward sign of a change in a white rat is that it is now a blue rat. When the animal is subsequently killed, the sections prepared from its tissues are found to be differentiated by the stain in a characteristic way; those of us fortunate enough to see the demonstrations which Prof. Goldmann gave before the Royal Society and the Physiological Society were struck, not only with the beauty of the

[5] 1912, **78**, 1. [6] 1912, B, **85**, 146.

preparations, but also with the usefulness of the new method in the elucidation of function. The dye can be administered either intravenously, intraperitoneally, or subcutaneously. The actual details of the technique, and the chemical constitution of the dyes mentioned and also of others which have been recently added to the list will be found described in full in the papers already quoted. What we are mainly concerned with here are the results.

The stain is embodied in the granules of specific cells throughout the body. Although it circulates in the blood, no blood corpuscle takes it up, nor has it any effect on the vascular lining. In the skin it is found in the fixed connective tissue cells, but chiefly in free cells in the lower layers of the cutis and subcutis. But these migratory cells appear also in every internal organ (except the nervous system), and always in connexion with interstitial fibrous tissue; they occur in muscles, glands, tendons, and especially in serous membranes. They have chemotactic irritability, and are phagocytic. On account of their affinity for pyrrhol-blue they were originally termed pyrrhol cells, and it seems probable that they originate in the bone marrow.

By means of intra-vitam stains one can further differentiate the Kupffer-cell of the liver, the reticulum cell of lymph glands and spleen, the interstitial cell of the testis, the follicular cell in the maturing follicles of the ovary, the cortical cell of the suprarenal, the epithelial covering of the choroid plexuses, and the cells which line the convoluted tubules of the kidney.

When pregnancy occurs in the stained animal, the appearance and behaviour of the placenta are most striking; the blue colour disappears from the skin, and is concentrated in the uterus, and in time the latter, forming a centre of attraction for the dye, ultimately dispossesses all the remaining tissues of their blue. In the uterus it is the free cells of the decidua serotina where the stain is mainly found. In quite early stages the stained cells penetrate into the primitive placenta and cast off their stained granules, which are snatched up by fœtal cells in the way nutritive material is. When once the placenta has attained maturity, however, the dye is found only in the fœtal cells which form the layer that separates the maternal and fœtal tissues. The embryo itself remains perfectly colourless, the stain not being able to penetrate this protective barrier. Further research has shown another important point; for the same cells which vigorously absorb the vital stain store also glycogen, fat, and hæmoglobin temporarily before these substances pass into the fœtal circulation. The avidity of such cells for the dye is thus connected with their functional activity in relation to really nutritive material; the importance of vital staining in embryological research is therefore apparent.

Equally important are its applications to pathological research. In the healing of wounds the pyrrhol cell appears on the scene after the initial emigration of leucocytes has taken place. It eats up the leucocytes or ingests the glycogen and fat which are derived from leucocytic disintegration. Eventually it becomes the spindle cell of the new connective tissue in the scar, and simultaneously loses its affinity, both for the blue dye and for fat stains.

In trichinosis the activity of the pyrrhol cell is prominently displayed; it wanders towards the uncapsuled parasites, passing in its way through lymphatic glands. The cells then spread into the interstitial muscular tissue, and finally, penetrating the sarcolemma, arrange themselves on the outer surface of the imprisoned trichinæ.

In tuberculosis a fundamental difference was discovered in the distribution of avian and bovine bacilli when grafted into the peritoneal cavity of the mouse. When bovine material is employed, it first causes extensive tuberculosis of the peritoneum itself, and the chief seat of further trouble is in the lungs, whither the bacilli are carried by the blood stream after penetrating the portal vein. The pyrrhol cells take no active part in this acute form of experimental tuberculosis. An entirely different result follows injection of the avian bacillus. The peritoneum and the organs within it show hardly any trace of the disease. The omentum, however, is full of blue patches, which are composed entirely of pyrrhol cells, the blue protoplasm of which is choked with myriads of bacilli. The liver, spleen, mesenteric glands, and to a less extent the lungs are also studded with similar aggregations of pyrrhol cells which have acted as phagocytes and so protect the animal from the disease. In the liver the Kupffer cells play a similar rôle. In the end, however, the protective action ceases, and the brave defenders succumb when the parasites increase still further. The pyrrhol cells then lose also their affinity for the blue dye, and show an increased affinity for fat stains, and finally disintegrate, allowing the bacilli to be distributed to the body generally *via* the lymphatic vessels, and not by the blood stream as in the case of the bovine bacilli.

In toxic degeneration of the liver produced by poisons such as phosphorus, the organisation after such non-inflammatory necrosis is attempted by vitally stained pyrrhol cells, which migrate along the liver lymphatics from the peritoneum towards the diseased tissues, and eventually assist in the repair of the damage.

Last, but not least, the new method appears destined to play a part in the elucidation of the mysteries of cancer and similar malignant growths. Here the aggregations of blue-stained pyrrhol cells attain extraordinary dimensions; they swarm round the growing tumour, penetrating it along its numerous blood vessels. In the

interior most of them succumb. It is just here that the interesting story stops, or is to be continued in Professor Goldmann's next? He is content to state that he at present regards the appearance of the blue cells as a specific local reaction induced by the tumour cell. No other migratory cell is attracted, and it may be that these cells are the bearers of nutriment. He has, however, already commenced some experiments on mouse tumour with Ehrlich's icterogen and sodium iodophenylarsenate. These poisons produce toxic degeneration of the liver, and are more powerful in this direction than phosphorus. The pyrrhol cells then absorb the degenerated products of the liver cells, preferably the bile-pigments, and transport them to the malignant growth. Hence the latter may wear both on its surface and in its interior a distinct yellow or jaundiced appearance. Since the tumour evidently suffers through the application, it does not seem improbable that the pyrrhol cell may also be active, or may be rendered active in transporting materials to the tumour which impede and even stop its growth.

It will be seen that this subject promises to become one of great importance from the biological point of view, and as time goes on the more specially chemical aspect of it will become clearer. The more strictly chemical side of the question, both in reference to the dyes themselves and to the method of their action on living cells, is treated in two interesting papers by W. Schulemann.[7]

Repair, Growth, and Synthesis in the Animal Body.

Our increased knowledge of the composition of proteins, the "flesh-forming" constituents of diet as Liebig termed them, has shown us that all of the members of that large group have very unequal powers in repairing the body waste. It is also now recognised that repair of the tissues which are fully developed is not the same thing as the active growth of the body which occurs before the adult stage is reached, and that food which is efficacious in the former may be quite ineffective in the latter condition. Recent work on metabolism has also shown that man cannot live on protein alone, even if it is mixed with fat and carbohydrate to supply the necessary energy, but that there are other organic compounds of uncertain nature which often in very small quantities are absolutely indispensable. Another general result of this renewed investigation has been the discovery that the animal body possesses a power of synthesising comparatively simply food material into more complex substances, which was previously considered to be the special feature of vegetable life.

I propose in the following section to illustrate these theses by

[7] *Arch. Pharm.*, 1912, **250**, 252, 389; *A.*, ii, 791, 859.

alluding to the more important papers in the year's output that support them.

In order to estimate the nutritive value of any article of food, experiments *in vivo* are absolutely necessary; no amount of mere chemical analysis or observations of digestion *in vitro* are sufficient, however useful they may be as accessory methods of research. The sort of work on the utilisation of individual proteins which is wanted is well illustrated by that of Mendel and Fine[8] on the proteins of various cereals and legumes. Mendel, in conjunction with Osborne,[9] has carried the matter further in their extensive experiments on rats, and shown that it is possible to keep these animals alive for prolonged periods (equivalent to the average life of the rat) when a single protein is the sole source of nitrogenous supply; and it is by means of such observations that they have reached the important conclusion that maintenance and growth are not the same problems. From the wealth of detail which is given to support this contention, I take but a solitary example, which is quite typical and obtained from the examination of an animal higher than a rat. A gliadin food mixture was given to a puppy in place of its mother's milk; this produced typical failure in growth, although the mother dog thrived on the same diet and actually produced young, and secreted milk in sufficient quantity and quality to induce normal growth in her offspring. No stronger proof could be adduced of a power to synthesise "Bausteine" in the body which are absent from the food. McCollum[10] makes the useful suggestion, seeing repair processes are of a different character from those of growth, that in cell katabolism and repair the processes do not involve the destruction and re-synthesis of an entire protein-molecule; this is obviously necessary during growth.

A similar power to synthesise lipoids from simple phosphorised compounds on a diet free from fats and lipoids was further determined by the same authors.[11] But restricting ourselves for the present to the question of proteins, one must allude next to a series of papers which deal with amino-acid synthesis and the chemical possibilities of the transformation within the body of one amino-

[8] *J. Biol. Chem.*, 1911, **10**, 345; 1912, **10**, 433; **11**, 1, 5; *A.*, ii, 63, 271, 272.

[9] *Proc. Amer. physiol. Soc.*, 1911, xii, *Amer. J. Physiol*, **29**. Full details in Publication 156, Part II, Carnegie Inst. of Washington, 1911; *A.*, ii, 271. *Zeitsch. physiol. Chem.*, 1912, **80**, 307; *A.*, ii, 957. *J. Biol. Chem.*, 1912, **12**, 473; *A.*, ii, 1190. The same note, namely, the different rôle of proteins in maintenance and growth, is struck by McCollum, *Amer. J. Physiol.*, 1911, **29**, 215; *A.*, ii, 63. For feeding on single proteins are also Rohmann, *Biochem. Zeitsch.*, 1912, **39**, 507; *A.*, ii, 462, and Osborne, Mendel, and Miss Ferry, *J. Biol. Chem.*, 1912, **13**, 233; *A.*, 1913, i, 124.

[10] See preceding footnote.

[11] Osborne, Mendel, and Miss Ferry, *J. Biol. Chem.*, 1912, **12**, 81; *A.*, ii, 779.

acid into another. The early members of the series were briefly mentioned in last year's report, and G. Embden[12] and his colleagues have continued the work, and supported their contentions by actual experiments *in vivo* (perfusion of liver, etc.). I do not propose here to repeat the details, the essentials of which have already appeared in our abstracts, but would merely point out that work of this kind is increasing by leaps and bounds our knowledge of the intimate processes of nutrition and metabolism, and demonstrates beyond cavil the wonderful synthetic powers which animal cells possess. The liver is credited with the bulk of the work, but this tendency to pile up hepatic duties is somewhat discounted by some researches to be alluded to a few paragraphs ahead. Another factor to be reckoned with is insisted upon by the American writers just mentioned, and that is bacterial action. It is quite possible that some of the new chemical permutations and combinations are the result of the activity of micro-organisms in the intestine; seeing that bacteria are always with us, this possibility cannot be neglected; but knowing also that it has been shown that healthy animal life is possible with a perfectly sterile alimentary canal, it is impossible to resist the conclusion that the tissue cells are more important than these accessory factors.

Loewi, Abderhalden,[13] and others alluded to in previous reports have shown that it is possible to maintain animals alive and in healthy equilibrium by feeding them on the simple "Bausteine" of the food if they are given in appropriate proportions. No one, however, would have ventured to prophesy that simple ammonium salts could replace amino-acids, or could be synthesised into tissue protein. This, however, appears to be probably true, and the year just passed is remarkable for a number of papers on this aspect of metabolism. The principal ones which deal with it are given in the footnote below,[14] but seeing that the subject is as yet in its infancy, one would perhaps be wise at present to adopt the cautious attitude of Abderhalden, who draws the general conclusion that although ammonium salts and especially the acetate influence the nitrogen balance, and may lead to the retention of nitrogen, never-

[12] *Biochem. Zeitsch.*, 1912, **38**, 393, 407, 414; *A.*, ii, 278, 279. See also Abderhalden and Hirsch on the formation of glycine in the organism (*Zeitsch. physiol. Chem.*, 1912, **78**, 292; *A.*, ii, 579.

[13] Striking recent experiments of this kind are given by Abderhalden, *Zeitsch. physiol. Chem.*, 1912, **77**, 22; *A.*, ii, 363.

[14] E. Grafe and Schläpfer, *Zeitsch. physiol. Chem.*, 1912, **77**, 1; *A.*, ii, 363; E. Grafe, *ibid.*, **78**, 485; *A.*, ii, 659; Völtz, *ibid.*, **79**, 415; *A.*, ii, 780; Abderhalden, *ibid.*, **78**, 1; *A.*, ii, 575; Abderhalden and Lampé, *ibid.*, **80**, 160; *A.*, ii, 956; Abderhalden and Hirsch, *ibid.*, 136; *A.*, ii, 957; *Ibid.*, **81**, 323; *A.* ii, 1189; Abderhalden and Lampé, *ibid.*, **82**, 21; *A.*, ii, 1191; Abderhalden and Hirsch, *ibid.*, 1; *A.*, ii, 1190; E. Grafe, *ibid.*, 347; *A.*, 1913, i, 125.

theless the assumption that animal cells can build up protein from ammonia and non-nitrogenous material (carbohydrate, etc.), is not yet proved up to the hilt; it is quite possible that the retained nitrogen may be in other and simpler combinations than protein.

Now let us return to the point about the part played by the liver in such syntheses. In several previous reports I have dealt with the question of protein absorption, and have throughout maintained the position that the complete (or almost complete) cleavage of proteins into individual amino-acids in the alimentary canal is followed by the absorption of these simple substances into the blood. Those which are of special importance in repairing the tissue waste are seized upon by the tissue cells to which the blood conveys them, and the unused residue is deamidised, and its nitrogen ultimately excreted as urea. Deamidation and formation of urea appear to be a special function of the liver, and has been generally assumed to occur rapidly. I have always strongly combated the idea to which Abderhalden among others has committed himself, namely, that re-synthesis of protein from the amino-acids occurs during absorption in the intestinal wall.

The work of 1912 has supported these contentions absolutely. In the first place, Folin and Denis[15] have published a most important set of papers which they have entitled "Protein metabolism from the standpoint of blood and tissue analysis." Folin is justly celebrated for the introduction of new and accurate analytical methods, and now his newly-introduced methods have been successful in proving that after the ingestion of proteins, or of amino-acids, it is perfectly easy to demonstrate and estimate an increase in the non-protein and amino-acid nitrogen of the blood. A new point made out is that deamidation does not occur so rapidly as we previously thought it did.

These observations have been criticised in two directions. Folin stated that a certain amount of nitrogenous absorption occurs in the stomach; London[16] considers this cannot be stated positively unless the remainder of the alimentary canal is excluded, for absorption from the auto-digestion of intestinal juices might conceivably be occurring. Folin,[17] however, has successfully defended his own point of view. After all, the point is only a minor one. Speaking personally, I am inclined to think that more accurate conclusions can be drawn from normal animals than from those with extensive mutilations such as London employs.

The other criticism comes from Abderhalden and Lampé,[18] who

[15] *J. Biol. Chem.*, 1912, **11**, 87, 161; **12**, 141, 253, 259; *A.*, ii, 271, 364, 780, 853.

[16] *Zeitsch. physiol. Chem*, 1912, **81**, 283; *A.*, ii, 1189.

[17] *J. Biol. Chem.*, 1912, **13**, 389; *A.*, 1913, i, 126.

[18] *Zeitsch. physiol. Chem.*, 1912, **81**, 473; *A.*, ii, 1190.

also deal with a minor point, namely, a question of chemical technique in the methods used. They suggest a modification for detecting amino-acids in the blood. The main importance of this apparently critical paper resides in the admission that after feeding an animal on meat or on proteolytic cleavage products the blood does contain excess of amino-acids which pass into it direct from the intestine. We can only hope that this means that Abderhalden now definitely abandons his view that protein synthesis occurs in the intestinal wall.[19] The same question is taken up by Buglia,[20] and he also arrives at the conclusion that synthesis of protein from its cleavage products does not occur in the wall of the intestine.

Let me conclude this discussion by some quotations from a paper by D. D. van Slyke,[21] which puts the problem very well, and shows that all physiological chemists throughout the world are falling into line in regarding the intestinal wall as no specific place for protein synthesis, and are also beginning to doubt whether the much-burdened liver has such multifarious duties as those it is usually credited with. He begins by describing a method for estimating amino-acid nitrogen in blood, for van Slyke, like Folin, is fertile in methods. By its use he shows that in fasting animals the amount of amino-acid nitrogen is 0·003—0·005 gram per 100 c.c. of blood. Absorption of 10 grams of alanine from the intestine increases this figure, and in the normal digestion of meat the amount may be more than doubled. The rapidity with which amino-acids disappear from the blood was illustrated by injecting 10 grams of alanine direct into the blood-stream; five minutes later only 1·5 grams were left in the blood, and 1·5 grams passed into the urine; so the remainder must have been taken up by the tissues. The theory that amino-acids are synthesised into blood-protein whilst passing through the intestinal wall therefore becomes superfluous, and there can be no doubt that they pass as such into the blood from the intestine, and then are rapidly removed from the blood by the tissues. The liver, moreover, appears to play no specially active part in picking up these acids; doubtless all the tissues help themselves. This conclusion is based on the observation that the blood of the femoral artery during digestion contains nearly as much amino-acid nitrogen as that in the mesenteric veins.

I have elected to devote most of the preceding paragraphs in this section to the proteins, but it must not be supposed that the

[19] That Abderhalden was weakening in this view was indicated in a previous paper (Abderhalden and Kramm, *Zeitsch. physiol. Chem.*, 1912, **78**, 382; *A.*, ii, 574). Here he states that his experiments do not contradict the theory.

[20] *Zeitsch. Biol.*, 1911, **57**, 365; 1912, **58**, 162; *A.*, ii, 182, 462.

[21] *J. Biol. Chem.*, 1912, **12**, 399; *A.*, ii, 1184.

problems of nutrition and of synthesis in the body are not also equally interesting in relation to carbohydrates and fats.

Exigencies of space, however, preclude more than a passing reference to these. In fact, I shall confine myself to two subjects only, one of which is connected with carbohydrate metabolism, and the other with one of those unknown but indispensable components of a healthy diet to which I referred in the opening paragraph of this section.

Glycolysis.—The disappearance of sugar from the body, and its ultimate oxidation with the formation of carbon dioxide and water, is a question of unusual interest, not only because the intermediate products are matters of discussion, but chiefly because the internal secretion of the pancreas is believed to play its part in glycolysis. Of the various tissue cells investigated by Levene and Meyer,[22] only one species hitherto has shown itself capable of causing glycolysis, lactic acid being an intermediate stage in the combustion of sugar; these cells are the leucocytes of the blood. It is, however, well known, as was first demonstrated by O. Cohnheim, that the combined action of muscular tissue and pancreatic extract causes sugar added to the mixture to disappear. Knowing, moreover, that sugar is the main source of muscular energy, the phenomenon was explained by supposing that the normal action of the internal pancreatic secretion on reaching the muscles was to facilitate the combustion of sugar; and the absence of that secretion after extirpation of the pancreas explained the accumulation of sugar and the occurrence of a diabetic condition. This view will certainly have to be revised in the light of Levene and Meyer's recent work,[23] if their discovery is confirmed, and one cannot at present see any flaw in their methods. The sugar certainly disappears, but it is not burnt up into oxidation products; in other words, sugar disappearance is not glycolysis in the usual acceptation of the term. The disappearance of the sugar is due to condensation into a polysaccharide, and the sugar can again be recovered after hydrolysis with acid. Here, indeed, we have a riddle that badly needs a guesser.

Accessory Factors in Normal Dietaries.—The reader will not have failed to notice in this report how largely America has figured in the research of the year. I attribute this largely to the wisdom of our Transatlantic cousins in providing adequate endowment for research, so that the ablest and keenest of American minds are attracted to devote themselves to what is under usual conditions unremunerative labour. My insular prejudices, however, lead me

[22] *J. Biol. Chem.*, 1912, **11**, 361; **12**, 265; *A.*, ii, 577, 852.
[23] *Ibid.*, 347; *A.*, ii, 577.

to congratulate myself that I am able in concluding this section to allude to an important metabolic research by a fellow-countryman. F. G. Hopkins was one of the earliest to recognise the importance of what for want of a better name we term the accessory factors in a dietary; and the effect of quite small quantities of such substances is admirably illustrated in his most recently published paper.[24] Groups of young rats were fed on a basal diet of caseinogen, fat, carbohydrate, and salts, and compared with other rats on the same diet plus a minute ration of fresh milk. The former soon ceased to grow; the latter grew normally. The consumption of food was practically the same throughout, but the milk addendum reduced the food necessary for a given increment in weight to one-half or less. Cessation of growth occurred before loss of appetite appeared. What the actual substances are in the milk which thus markedly, although in a secondary way, affect growth is not yet known.

Beri-beri. Polyneuritis.

The importance of minute quantities of certain materials in the diet is well exemplified in the causation of that terrible disease of the East known as beri-beri. The interest of the subject leads me to supplement what I said last year on this disease, and to break through my usual rule in not taking up the same subject two years in succession. It may now be taken as proved that the disease is usually produced by a diet of polished rice, that is, rice deprived of its outer layer in which the anti-neuritic substance occurs. It can be cured by the administration of the polishings, or of the active substance separated from them. The rapid progress made in the discovery of the cause, and the cure of the condition illustrates the usefulness of animal experimentation, for the disease can be easily caused in birds, and now it can be as easily cured. C. Funk, who was the first actually to separate out the anti-neuritic principle, which he terms *vitamine*, has not yet fully made out its chemical composition, but he states in his latest paper[25] that its properties suggest it is a pyrimidine base, and forms a constituent or derivative of nucleic acid. For curing pigeons of polyneuritis, doses of 0·02 to 0·04 gram given by the mouth are sufficient. The same base he also separated from yeast, ox-brain, milk, and possibly from lime-juice. Schaumann's hypothesis that a deficiency of organically combined phosphorus in the food leads to a similar poverty of phosphorus in the body, and thus to neuritis is therefore

[24] *J. Physiol.*, 1912, **44**, 425; *A.*, ii, 779.
[25] *Ibid.*, 1912, **45**, 75; *A.*, ii, 856.

not confirmed, and H. Wieland[26] arrives at a similar conclusion from his experiments on mice.[27]

Moore, Edie, and others[28] at Liverpool have also separated out the base, and have used yeast as the material to work with. They suggest the name *torulin*. On treatment with barium hydroxide it gives off trimethylamine, and they ascribe to it the formula $C_7H_{16}O_2N,HNO_3$. They are, however, continuing the investigation, and the elucidation of the actual chemical composition of the base can only be a matter of time. The important practical point is that its existence and action have been proved.

The amount of vitamine in various articles of food has been determined by ascertaining how much of each must be added to a diet of polished rice in order to prevent in birds the occurrence of polyneuritis.[28a] It was found that the anti-neuritic material is irregularly distributed amongst the foodstuffs; thus 20 grams of beef daily were necessary; about half this amount of sheep's brain proved to be sufficient, and among the animal foods examined egg-yolk was the most efficient, 3 grams being the necessary daily dose. Amongst the vegetable foods, the efficiency of lentils and unhusked barley were about equal to egg-yolk, but, of all others, yeast was the most efficient in preventing the disease, only 0·5 gram being enough.

The question will doubtless be asked, especially by sufferers from neuritis, is this discovery of any use to them. The proof of the pudding will be the eating thereof, and there appears no reason why they should not try. Vitamine is, at any rate, quite harmless, but whether it will be of widespread therapeutic value is another question. A cure which is scientifically sound is one that removes the cause of the ailment. In beri-beri, a disease due to lack of the base, the cure by the administration of the base is therefore only common sense. But neuritis is caused in other ways, by pressure on a nerve, by inflammation of the sheath of the nerve, and so forth. There is no reason to believe that in this country the sufferers have been on a diet free from or even poor in this particular substance. So that although we may hope that the giving of the drug may assist in alleviating the condition, it does not strike at the root of the mischief, and so one must be very cautious in holding out hopes of any great relief.

[26] *Arch. expt. Path. Pharm.*, 1912, **69**, 293; *A.*, ii, 962.

[27] The contradictory results of observers in their attempts to cure polyneuritis with lecithin is due to the fact that lecithin is often contaminated with vitamine when prepared from animal organs (H. Maclean, *Bio-Chem. J.*, 1912, **6**, 355; *A.*, ii, 1192).

[28] *Bio-Chem. J.*, 1912, **6**, 234; *A.*, ii, 794.

[28a] E. A. Cooper, *J. Hygiene*, 1913, **12**, 436.

A very remarkable case of beri-beri has recently been described by V. L. Andrews,[29] in which rice played no part. It occurred in a suckling infant of a Philippine mother, and was cured by withholding from it the milk of its mother. Analysis of the milk showed nothing noteworthy in its general composition; the calcium and phosphorus were even higher than usual. Yet there must have been a failure of some substance in the milk, presumably of the vitamine, which is a normal constituent of that fluid; young dogs were fed upon it, and all of them developed peripheral neuritis, œdema, and dilatation of the right side of the heart; in fact, all the symptoms typical of beri-beri.

Such cases as this widen the outlook and form a useful commentary on the remarks just made concerning the multiplicity of causes that may lead to the development of the neuritic condition.

In concluding this section, I may mention the very useful term "deficiency diseases," introduced by Funk for beri-beri, scurvy, pellagra, and a few other pathological conditions due to defective diet.

Coagulation of the Blood.

The theory most in vogue at present to account for the phenomenon of blood-clotting is that of Morawitz; and this theory is an amplification of Hammarsten's, which in its original form postulated the existence of two factors; one of these is fibrinogen, a protein substance in solution in the blood-plasma, and the other is an agent which is liberated by the disintegration of the corpuscular elements of the blood, and which on account of its enzyme-like characters was called fibrin ferment, or thrombin. The action of thrombin on fibrinogen resulted in the formation of fibrin from the latter. Hammarsten even in his earlier papers noted that calcium salts favoured congulation, and the prime importance of such salts was fully demonstrated by the subsequent work of Pekelharing, Arthus, and others, who showed that coagulation could be entirely prevented by decalcifying the blood by the addition of small quantities of a soluble oxalate. The analogy between blood-clotting and milk curdling by rennet suggested that the part played by calcium in both processes was identical. It has been proved that the clot in milk is a calcium caseate, and at first it was supposed that fibrin was a calcium compound of fibrinogen. But it was soon found that this is not the case. The part played by calcium in the clotting of blood is in the production of the thrombin, and not in the subsequent action of thrombin on fibrinogen. Like other enzymes, thrombin has an inactive procursor, which has received

[29] *Philippine J. Sci.*, 1912, **7**, 67.

the name of prothrombin, and what the calcium does is to convert this zymogen into the active enzyme.

Fibrinogen, prothrombin, and calcium are not, however, the only three agents which participate in the phenomenon; and it was the special feature of the theory of Morawitz that he assumed the existence of an organic activator which has since received several other names, but which is usually spoken of as thrombokinase. Much in the same way as the inactive trypsinogen of the freshly secreted pancreatic juice requires to be activated by the enterokinase of the intestinal juice, so it is supposed that the thrombokinase acts in conjunction with calcium in the liberation of thrombin from its mother substance prothrombin. Thrombokinase or an analogous substance is also provided by the disintegration of other tissues. It is well known that if blood when shed is allowed to come in contact with other tissues, such as the muscles and skin which are cut through, its coagulation is hastened. Even although this is prevented by collecting the blood straight from an artery through a clean glass tube, it clots in time, and so the thrombokinase which is assumed to be necessary was further assumed to originate from the blood-corpuscles.

Of the four fibrin factors, two therefore are present in the fluid part of the blood, namely, fibrinogen and the calcium, and the other two (prothrombin and thrombokinase) are furnished by the corpuscles, and especially by the blood-platelets.

About this date, researches on immunity were in full swing, and the ideas current in that region of work were reflected in the theories put forward concerning the action of enzymes generally. The matter was therefore complicated by the discovery of anti-enzymes. The special one in the blood which keeps it fluid under living conditions was dubbed anti-thrombin, and according to some observers, the assumption of an anti-kinase was also necessary.

Whether the blood remained fluid, or set into a coagulum was therefore the resultant of the action of opposing forces, some of which favour the interaction of thrombin and fibrinogen, and others of which inhibit that action.

Quite at an early stage in the development of these new ideas Leo Loeb [30] put forward other views, especially in relation to the part taken in the process by tissue extracts, and he considered that the coagulins of the tissues as he termed them were not merely activators, but entered into the actual process of fibrin-formation.

An entirely new note in criticism was struck by Rettger, who worked with Howell, and subsequently by Howell [31] himself. These observers put forward grounds for believing that thrombin is not

[30] See *Ann. Report*, 1905, 180.

[31] *Ibid.*, 1910, 189.

an enzyme after all, for they found a definite quantitative relationship between the interacting substances, a fact which is not in accord with the conception of the ferment-like character of thrombin, and during last year H. Stromberg[32] supported Howell's view. The idea that thrombin is not an enzyme has provoked much reflection and criticism among physiologists, although, so far as I know, no one has yet got so far as to repel or even attack it in print. A complicated question of this kind is not susceptible of academic discussion without facts to go upon, and facts take time in working out. So far, however, physiologists as a whole are not yet convinced, and still teach that thrombin is an enzyme. If in fibrin formation we had only to deal with two reacting substances, thrombin and fibrinogen, the problem would be a simple one, and could be easily settled, but when the factors are more numerous the difficulties are increased. It is admitted by all that thrombokinase under one or other of its numerous aliases, whatever may be its action, is not an enzyme, and it may be that it was the action of this substance which complicated Howell's results.

The papers on the subject, published in the year 1912, have mainly emanated from Baltimore; thus Meek[33] has taken up the question of seat of origin of fibrinogen. Dogs were bled, the blood whipped, and then re-injected minus its fibrin. The regeneration of fibrinogen occurred with great rapidity, 100 per cent. increase being noted in three hours. If the liver was entirely excluded from the circulation, however, regeneration did not take place at all, and the small amount of fibrinogen left in the residual blood rapidly disappeared. A hasty observer would have at once jumped to the conclusion that the liver itself forms fibrinogen, but experience breeds caution, and, as Dr. Meek states, there is still open another possibility, namely, that the liver may influence the formation of fibrinogen elsewhere by means of a hormone.

The work of Bayne-Jones[34] emphasises the importance of the blood-platelets in providing the corpuscular contribution to fibrin formation. He found in his experiments with platelets and pure solutions of fibrinogen that the former contain a substance, prothrombin, which after activation with calcium, clots fibrinogen. This is a confirmation of Morawitz's views. He also found that extracts of platelets cause the clotting of "peptone plasma," a

[32] *Biochem. Zeitsch.*, 1911, **37**, 177; *A.*, ii, 59.

[33] *Proc. Amer. physiol. Soc.*, 1911, xix, *Amer. J. Physiol.*, **29**; *A.*, ii, 273.

[34] *Amer. J. Physiol.*, 1912, **30**, 74; *A.*, i, 459. Cramer and Pringle reached the same conclusion by a different method, for they found that after removal of the platelets by filtration through a Berkfeld filter from oxalate plasma, coagulation can no longer be induced by the addition of calcium salts (*Proc. physiol. Soc.*, 1912, xi, *J. Physiol.*, **45**).

form of plasma which already contains thrombin, fibrinogen, and calcium. The platelets are therefore the source of the fourth factor, which Morawitz would term thrombokinase, but which Bayne-Jones, using Howell's nomenclature, prefers to call thromboplastin. He explains the absence of clotting in peptone blood as due to the presence of large amounts of anti-thrombin, and the action of thromboplastin is to neutralise the antithrombin.

The question of antithrombin also is taken up by D. Davis.[35] He found, as many have found before him, that injection of thrombin into the blood-stream within certain limits does not produce intravascular coagulation, and considers that the injection excites the rapid formation of its antidote, the agent which normally prevents clotting during life.

The general idea that thrombokinase is not an activating agent, but is the antagonist of antithrombin, is more fully advocated by Howell,[36] under whom both Davis and Cecil worked. Later in the year[37] he brought forward some more evidence in favour of this view, and supplemented it by hazarding an opinion of the actual nature of thromboplastin. He considers that it is a phosphatide of a nature akin to kephalin. He thus revives an old notion originally promulgated by Wooldridge many years ago. When Wooldridge worked our knowledge of the phosphatides and lipoids generally was very scanty, and the nucleo-proteins were almost unknown. When, therefore, Wooldridge spoke of lecithin as a help to blood-clotting, he exercised not only a tenable view of the process, but if Howell is correct he showed a truly prophetic instinct.

Quite independently of Howell and his pupils, much the same view has found favour with E. Zak.[38] He finds that a diminution of the lipoids of the plasma leads to a delay in its coagulation, and that the addition of phosphatides from other organs acts even more strongly in hastening coagulation than those normally present in the blood. Alkaloids which unite with lecithin are also inhibitory to coagulation. Such results agree with the views of Alexander Schmidt on zymoplastic substances, and if correct render the assumption of a kinase in Morawitz's sense unnecessary.

We thus see that the problem of blood-clotting has entered on a new phase, and is in a more interesting condition than it has been in for many years past.

[35] *Amer. J. Physiol.*, 1911, **29**, 160; *A.*, ii, 60. A paper preceding this (*ibid.*, 156; *A.*, ii, 60) by Cecil contains many valuable hints for the purpose of obtaining and preserving peptone plasma and thromboplastic extracts.

[36] *Ibid.*, 187; *A.*, ii, 60.

[37] *Ibid.*, 1912, **31**, 1; *A.*, ii, 1078.

[38] *Arch. expt. Path. Pharm.*, 1912, **70**, 27; *A.*, ii, 1065.

Oedema.

The œdematous or dropsical condition is due to an abnormally large formation of lymph, the fluid which leaks from the blood as it passes through the thin-walled capillaries, and is thus an exaggeration of a normal process. It can be produced by an increase of the capillary pressure, as when one ties a ligature around a limb so as to obstruct the venous outflow. It can be also produced by an injury to the capillary epithelium, which renders the vessel walls more leaky. Another factor is doubtless a change in the blood, such as an increase in its water, or the development of poisons which, circulating in the blood, lessen the vitality of the capillary walls. Carl Ludwig taught that increased lymph formation was the result of purely physical factors of this nature, and the same position has more recently been maintained by Starling. Heidenhain introduced the so-called "vital theory," in which he bestowed upon the living cells of the capillary wall a selective power which enables them actually to secrete lymph; he was further the inventor of the word lymphagogue (or lymph driver), which he applied to various chemical agents, many of which he considered increased the lymph by stimulating the capillary cell to heightened secretory activity. Pathologists have for long wrangled over the question of the relative merits of the mechanical and vitalistic hypotheses, and the mechanical theorists have differed according as to whether pressure variations, cell-permeability, or blood changes such as hydræmia are the more potent in the causation of the condition. Non-partisan onlookers have agreed that in different cases these various factors may have different values, and although most exhibit scepticism regarding Heidenhain's extreme views, they are nevertheless quite open to conviction that the cells may possibly exercise, thin though they are, a certain amount of selective action.

In 1910, however, Martin Fischer, of California, published a book [39] which rather fluttered the dovecotes of the pathologists, for it denied that any of the factors mentioned were of any real consequence at all, or, at any rate, were quite insignificant in comparison with a new power which he considered his experiments taught him was the main motive force in attracting fluid from the blood into the tissues. He found by experiments on various colloids that acidity caused them to swell more when immersed in watery fluids than when the reaction was neutral. Dead frog's legs which had become acid similarly absorbed more water; and put in barest

[39] "Œdema," S. Wiley and Sons, New York. See also *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 159; *A.*, 1911, ii, 309; *Koll. Chem. Beihefte*, 1911, 2, 304; *A.*, 1911, ii, 510.

outline his theory of œdema is that increase in the acidity of the tissues which is the result of many pathological processes causes by osmotic pressure water to be drawn from the neighbouring blood-stream. I think physiologists all felt when they read Fischer's very clear and well-argued statements that here, at any rate, was a new light on what is certainly a puzzling problem, but they were not prepared to accept fully the sweeping conclusions he drew. A palpably weak point that immediately attracted notice was the admission that an alkaline reaction was almost as potent as an acid one in promoting the swelling of colloids; and I fancy many felt that the experimental data were hardly sufficient to support all his contentions. During the present year several papers have appeared which contest the new views; for instance, Pincussohn [40] found that many tissues behave exactly in the contrary way towards acid from what Fischer found. Gelatin, muscle, and cartilage swell more in acid, but liver, spleen, kidney, and lung do not. It is quite evident that a rule which is not universally true cannot be of prime importance. A. R. Moore [41] is still more positive that Fischer is incorrect. Gies [42] severely criticises the theory, while he does not deny the possibility that tissue changes may have an influence; he takes the view that protein cleavage products, the result of the action of tissue proteases, may be efficient water attractors, but admits that up till now this has not been proved. Fischer [43] has defended his views, but the attack upon them has been sufficiently serious to make physiologists doubtful whether they can be accepted without very considerable reserve.

I take the present opportunity of correcting a slip that occurred in my report of last year. Speaking of *acapnia*, I stated that the word had been introduced by Dr. Yandell Henderson. Dr. Henderson has certainly made the word familiar, but as has been pointed ont to me, he did not himself coin it. The late Professor Angelo Mosso, of Turin, was the author of the word; in his "Life on the High Alps" (1898) he says: "As the ancients were not acquainted with carbonic acid, and had therefore no name for it, I chose the word smoke as most resembling it in a physiological sense, and so coined the word 'acapnia,' which means without smoke."

W. D. Halliburton.

[40] *Zeitsch. expt. Path. Ther.*, 1912, **10**, 308; *A.*, ii, 666.
[41] *Pflüger's Archiv*, 1912, **147**, 28; *A.*, ii, 856.
[42] *Biochem. Bull.*, 1912, **1**, 461; *A.*, ii, 856; *Ibid.*, 540; *A.*, ii, 1080.
[43] *Zeitsch. Chem. Ind. Kolloide*, 1912, **10**, 283; *A.*, ii, 784; *Biochem. Bull.*, 1912, **1**, 441; *A.*, ii, 856.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

The year 1912 represents a period of steady progress without any remarkable discovery or new advance to make the date memorable in the history of the science. It is perhaps hardly to be expected that any wide new generalisation can be attained for some time to come. The first approximations to the truth have already been made, and we are at present realising the inadequacy of the analytical methods available to solve the very intricate questions involved in all living processes. In every direction, in the chemistry of the soil, in the nutrition of the plant and of the animal, evidence is accumulating of the powerful effects of traces of this or that constituent, traces which are both minute and difficult to identify in the complexes of which living tissue is composed. Perhaps the most striking example is afforded by recent work in animal nutrition. The older investigators were concerned with the broad quantitative facts concerning the utilisation of food —proteins to repair nitrogenous waste—carbohydrates, and fats as sources of energy. It has now been shown, however, that an animal may be supplied with a diet perfectly balanced from this point of view, pure proteins, carbohydrates, fat, and salts in adequate quantities, and will yet fail to grow or even to thrive unless a minute trace of some materials directly derived from living organisms, such as meat extract, milk, or fresh vegetables, is given. The amount of the latter constituent involved do not enter into the quantitative statement of the food supplied and utilised, yet they are indispensable to the well-being of the animal. Again, in discussing the chemical processes taking place in the plant, we must admit that we can follow no one of them accurately because of the imperfection of our analytical methods. The fundamental function of the plant is photo-synthesis and the subsequent migration and storage of the carbohydrates produced thereby; in order to follow the sequence of this process it is necessary to estimate with accuracy the constituents of a mixture containing five- and six-carbon sugars, bioses, starch, and other carbohydrates approximating to starch, all in dilute solution and liable to change from the presence of

enzymes, masked also by the presence of nitrogenous substances of various stages of complexity. Until analytical methods have been worked out capable of dealing with such complexes as this, and with reasonable rapidity, we can neither follow the development of the plant nor reason about such practical aspects as its quality or food value.

Soil Chemistry.

The question of the increased fertility of soils that is produced by heating to the temperature of boiling water or exposure for a time to the vapour of antiseptics has continued to occupy the attention of investigators in all parts of the world. Russell and Hutchinson have so far published no further communication regarding their theory of the source of the increased productivity, namely, that it is due to the destruction of a factor that inhibits the free development of the bacteria reducing the compounds of nitrogen present in the soil to the state of ammonia, which factor consists in certain forms of protozoa inhabiting normal soil; but none of the other investigations invalidates their theory. Russell, in collaboration with F. R. Petherbridge,[1] has published an account of experiments on the treatment of greenhouse soils on a commercial scale both by heating with steam and by the addition of various antiseptics. In the rich composts employed by market gardeners under glass, which are constantly maintained in a very moist condition and at high temperatures, deterioration sets in after a few years, and the soil has to be changed, although analysis would still show it to be rich in all the elements of plant food. The conditions are obviously such as would favour the development of protozoa, but nematodes and other parasitic organisms also increase abnormally and are affected by the treatment just like the protozoa. The authors found that such greenhouse sick soil can readily be restored to its former condition and made even more productive by steam heating or by the addition of small quantities of various antiseptics, of which formaldehyde is the most practically effective. Methods have been worked out which are commercially remunerative, and many of the market gardeners growing tomatoes and cucumbers are now partly sterilising their used soils as a matter of business routine. The question, however, calls for much more investigation, as heating to such temperatures as 100° produces substances which persist in the soil for a time and are injurious to seedlings and the earlier stages of certain plants, although not to others. The formation, however, of these injurious bodies is most irregular, and the results cannot as yet be predicted with any particular soil.

[1] *J. Board Agriculture*, 1912, **18**, 1913; **19**, 809.

O. Schreiner and E. C. Lathrop[2] have isolated some of these soluble substances that are formed in steam-heated soils. They took two soils of the same type, one poor and the other rich. From the poor soil they obtained dihydroxystearic acid and various decomposition products of nucleic acid, namely, xanthine, hypoxanthine, guanine, cytosine, arginine, all of which substances were increased in amount by the heating process. In the rich soil they were not present at the outset, but were produced by heating. The nitrogen compounds may serve as food for plants and add to the value of the soil, but this value is overbalanced by the detrimental effects of the dihydroxystearic acid, which must be removed before the benefit of steaming is realised. E. C. Lathrop, in another communication,[3] explains his method of isolating guanine, which has so far only been found in heated soils, probably because it is so subject to destruction by the micro-organisms, etc., present in normal soil. Among the most effective compounds examined by Russell and Petherbridge was calcium sulphide, to which they are inclined to attribute the fertilising value of the old form of "gas lime" known as "Blue Billy," and E. Boullanger[4] finds the addition of flowers of sulphur increases the fertility of the soil. As this increase is not obtained with soil that has been sterilised, Boullanger concludes that the action of the sulphur must be in some way concerned with the living organisms of the soil. In a further paper,[5] he attributes to the sulphur an activating effect upon the organisms breaking down the insoluble nitrogen compounds of the soil, because only small doses are effective, further additions reducing the fertility of the soil below the normal. A. Demolon[6] considers that the presence of free sulphur in crude ammonium salts from the gas works explains the manurial efficiency of these compounds, which is greater than can be attributed to the nitrogen alone that they contain. It would hardly seem, however, that any very trustworthy evidence has been produced of the activation of bacteria by non-nutritive substances. The whole question of so-called "catalytic" stimulus of either lower organisms or plants is still enveloped in doubt as to the facts to be explained.

It is satisfactory to note that considerably increased attention is being paid to liming soils both in practice and in the investigation of the effects of lime on the chemical and bacteriological changes in the soil. At one time among the most widespread of farming operations, liming and chalking fell into disuse with the rise in

[2] *J. Amer. Chem. Soc.*, 1912, **34**, 1242; *A.*, ii, 981.
[3] *Ibid.*, 1260; *A.*, ii, 982.
[4] *Compt. rend.*, 1912, **154**, 369; *A.*, ii, 381.
[5] With M. Dugardin, *ibid.*, **155**, 327; *A.*, ii, 971.
[6] *Compt. rend.*, 1912, **154**, 524; *A.*, ii, 382.

the cost of labour and the introduction of artificial manures, and it is only recently that their value, indeed necessity, on many soils is beginning again to be recognised. In two extensive papers, O. Lemmermann, A. Einecke, and H. Fischer[7] discuss the effect of lime and magnesia in various ratios on the bacterial content and activity of the soil, and the effects that may be observed on plants arising from either the presence or the lack of this constituent. P. E. Brown[8] discusses the effect of applications of ground limestone up to the rate of three tons per acre on the Wisconsin experimental plots. He finds that the base increased the number of bacteria present in the soil; at the same time its ammonia-making, nitrifying, and nitrogen-fixing powers had all been raised. As might be expected, the crop-producing powers of the soil had been raised *pari passu*.

E. Blanck[9] has examined the laterite soils of the tropics and compared them with the red soils of temperate countries, such as those derived from the Permian and the Triassic formations. His analysis would point to considerable similarity between the two sets of soils, although the surface of the laterite soils in proportion to the amount of silica and alumina they contain is greater, because the sesquioxides are partly in a colloidal state. D. J. Hissink[10] points out that Blanck's analyses indicate a much higher ratio of alumina to silica in the laterite than in the red soils, van Bemmelen having previously noted the high proportion of free alumina as a characteristic of laterite soils.

As regards the study of soils *in situ* a survey of the soils and agriculture of Shropshire has been published by G. W. Robinson,[11] and contains a number of analyses, chemical and physical, of soils derived from the Old Red Sandstone, the Wenlock Shale and other Silurian rocks, and from the Bunter and Keuper. A. D. Hall and E. J. Russell[12] report studies of the composition of the soil and of the grass growing on them of certain fields in Romney Marsh, where some fields are capable of fattening six or eight sheep to the acre in the summer months, whereas the land alongside, however lightly stocked, will only maintain the sheep in a growing condition. Three pairs of such fields were studied, but despite the great differences in their productivity, the ordinary methods of analysis, mechanical and chemical, did not reveal any marked causal factor which would differentiate between them. In

[7] *Landw. Jahrb.*, 1911, **40**, 174, 255; *A.*, ii, 198.
[8] *Centr. Bakt. Par.*, 1912, ii, **34**, 148; **35**, 234; *A.*, ii, 670.
[9] *J. Landw.*, 1912, **60**, 59; *A.*, ii, 482.
[10] *Ibid.*, 237; *A.*, ii, 981.
[11] Published at Shrewsbury.
[12] *J. Agric. Sci.*, 1912, **4**, 339.

each pair the soil of the good and the bad field, although differing in type in the three cases studied, was similar within the limits of error of the method, the water content and temperature throughout the growing season were also similar, and the herbage neither botanically nor chemically could be distinguished. The only constant and significant differences found were that the good soils were slightly higher from the permanent water table, more permeable to water, and richer in phosphoric acid, although the poorer soils could not be regarded under ordinary standards as deficient in this constituent. The soils of the good fields were also more active, their oxidising power and the rate at which they produced nitrates and ammonia were greater. The herbage was characteristically more leafy and less stemmy on the good fields, but the proportions of fibre and of nitrogen compounds —protein, non-protein, and digestible—revealed no significant differences. The general conclusions reached by the authors were that our existing methods of analysis, both of soils and of fodder, are not refined enough to discriminate between good or bad in cases of this kind.

Bacteriology.

One of the most important processes in the bacteriology of soil constituents has hitherto received remarkably little attention, despite the fact that it plays a considerable part in other industrial processes. We refer to the fermentation of cellulose and other insoluble carbohydrates found in plant tissues. The broad facts that such substances are rapidly oxidised in soil to carbon dioxide, and that humus, methane and hydrogen are possible by-products, have long been familiar, as also that the degradation process is a biological one, but the investigations of the agencies are few and incomplete. Omelianski has described two organisms which work under anærobic conditions and in addition to carbon dioxide, fatty acids and humus produce, the one methane, the other hydrogen, but few other investigators have continued on this line of research. K. F. Kellerman and L. G. McBeth[13] have now published a preliminary account of a fresh attack on the cellulose organisms, which already leads us to revise our conclusions on the subject, and brings them much more in accord with field experience. Unable to isolate organisms agreeing with those described by Omelianski, they obtained from him preparations of the bacteria he had described, and were able to isolate two distinct cellulose ferments from the methane-forming, and one from the hydrogen-forming, preparation. All three, however, proved to be only facultative

[13] *Centr. Bakt. Par.*, 1912, ii, **34**, 485.

anærobes, which oxidised cellulose most readily in the presence of oxygen. In no case, however, did the pure culture of the organism give rise to gas; both the methane and the hydrogen were liberated by contaminating organisms from the products of the degradation of the cellulose. These investigators also succeeded in isolating from soil eleven other organisms attacking cellulose, one of which belonged to the thermophilic group. All these acted as facultative anærobes, and none of them gave rise to gas. Large numbers of fungi were also found to have the power of dealing with cellulose.

With the above exception, bacteriological investigation seems latterly to be concerned more with the soil as a whole, with the activity of groups of organisms bringing about a particular change, than with the work of particular organisms isolated under laboratory conditions. The view that the ammonia-making bacteria in the main determine the formation of available nitrogen compounds, and in consequence the fertility of the soil, is gaining ground, and is strengthened by several of the researches that have been published during the year. It was long held that the higher plants could only take up nitrogen from the soil in the form of nitrate, and after the discovery of the nitrifying organisms, it became customary to regard the rate of nitrification in the soil as the limiting factor in supplying the crop with nitrogen. As, however, the amount of ammonia in the soil never increases beyond very low limits unless the nitrification organisms have been killed off by one of the processes of partial sterilisation, it becomes evident that nitrification normally goes on as fast as ammonia can be supplied, and that the limiting factor is the rate at which the organisms splitting off ammonia from the nitrogenous residues do their work, rather than the activity of the further group which converts ammonia into nitrates. Other evidence has shown that the nutrition of the plant by ammonia instead of nitrates takes place to a considerable extent in the field, and is not a matter of abnormal laboratory conditions. In this connexion attention may be drawn to a paper by P. E. Brown and R. S. Smith,[14] who have been investigating the bacterial activity of the soil at different seasons of the year, and especially after freezing has taken place. In autumn, the number of bacteria diminishes with the fall of temperature, but rises again rapidly after freezing has taken place. The ammonia-making, the nitrifying, the nitrogen-fixing, and the denitrifying power of the soil all show the same sequence, but the rise of activity is most marked in the ammonia-making power. The authors conclude that the increase in the numbers of bacteria must take place when the soil is frozen, but they do not seem to have

[14] *Centr. Bakt. Par.*, 1912, ii, **34**, 369.

considered whether it may not follow very quickly on a liberation of soluble food brought about by the freezing. In dealing with plants, we have evidence that processes like freezing, by altering the water content of the cells, brings enzymes into play and starts or speeds up many actions which result in soluble products leaving the cell, and by analogy one may well expect something of the same kind to take place in the soil, just as exposure to chloroform vapour increases the soluble constituents that can be obtained from the soil.

P. E. Brown[15] has also traced the effect of the rotation of crops on the bacterial state of the soil. He found a larger bacterial content and increased activity in ammonia making, nitrification and nitrogen fixing, in soil that had been under a rotation as compared with soil that had been continuously cropped with one plant. The soil of plots under a long rotation again gave better results than that of land under a short rotation of two or three crops only. Curiously enough, where a green crop had been turned in there was sometimes a decrease in the nitrogen content, but this the author is inclined to attribute to the reduction of the moisture brought about by the growth and ploughing in of the green crop. These facts must be considered in connexion with recent theories on the cause of the benefits due to rotations.

Another interesting field study of the bacterial changes in soil is reported by R. Stewart and J. E. Greaves,[16] who for some years have been determining the nitrates in a rich soil well supplied with calcium carbonate under irrigation in California. They found that the irrigation water increased the production of nitrates, but the smaller quantities of water were more effective than the larger applications. Again, the amount of nitrate varied very markedly with the depth, and successive layers of soil, although thoroughly moist, could contain very different proportions of nitrate. A zone rich in nitrate could be made to rise or fall in the soil, but apart from these vertical movements there was little or no diffusion, and no evidence that any soil solution of approximately uniform composition, as postulated by Whitney and Cameron, was ever formed. Different crops had very varied powers of seizing on the nitrates when formed; lucerne (alfalfa) and oats always kept the proportion of nitrates and the concentration of the soil solution very low as compared with potatoes and maize. In spring the nitrate content of the cropped soil was higher than that of the fallow; in autumn the reverse was true, as had previously been observed by Warington and King. Vogel[17] has been considering the

[15] *Centr. Bakt. Par.*, 1912, ii, **35**, 234.
[16] *Ibid.*, **34**, 115.
[17] *Ibid.*, 540; *A.*, ii, 1089, 1206.

destruction of nitrates in the light of certain experiments in which the soil was placed in shallow layers in porcelain vessels. The soil contained 15 to 20 per cent. of water, but although no fresh organic matter was present, great losses of nitrates were experienced up to 60 per cent. within ten days. The reduction seems to depend on the exclusion of air by the moisture in the little aggregates of soil. The author suspects some purely chemical reduction of nitrate, but the evidence against biological action does not seem very strong.

C. B. Lipman and L. T. Sharp[18] have investigated the toxic effects of various substances, chloride, sulphate, and carbonate of sodium, found in alkali soils, on the activity of the ammonia-forming, nitrifying, and nitrogen-fixing organisms. The nitrogen-fixing organisms, unlike those causing nitrification, are resistant to comparatively high concentrations of sodium chloride and sulphate, hence the abnormal accumulation of nitrates observed by Headden and Sackett[19] might still be due to bacterial action. The explanation advanced that the accumulation was due to exceptional fixation of nitrogen by *Azotobacter* had been criticised, not only on the score of the absence of carbohydrate as a source of energy for the nitrogen fixation, but also on the ground that the chlorine in the soils increased with the nitrate to such an extent as would inhibit bacterial action, a correlation which would also indicate leaching and seepage as the source of both salts.

J. Stoklasa[20] has studied the biological absorption of various manure constituents when added to soils. When solutions of soluble phosphates, potash, ammonia salts or nitrates are allowed to percolate through the same soil, sterilised in the one case and not in the other, there is always considerably greater removal of the fertilising constituent by the unsterilised than by the sterilised soil. The bacteria either utilise the material in growth and multiplication, or arrest it in some way by temporary adsorption. Stoklasa regards the amount of absorption as proportional to the number of bacteria in the soil, and proposes to take it as a measure of the bacterial content, and therefore of the fertility of soil. A. Duschetschkin[21] also demonstrates the biological precipitation of phosphoric acid when solutions are placed in contact with a black soil enriched with starch. If the soil is first sterilised, the phosphoric acid remains soluble.

[18] *Centr. Bakt. Par.*, 1911, ii, **32**, 58; 1912, **33**, 305; **35**, 647; *A.*, ii, 76, 473, 1200.

[19] *Ann. Report*, 1911, 222; Sackett, *Centr. Bakt. Par.*, 1912, ii, **34**, 81; *A.*, ii, 670.

[20] *Chem. Zeit.*, 1911, **35**, 1425; *A.*, ii, 198.

[21] *J. Exp. Landw.*, 1911, 666; *A.*, ii, 677.

Chemistry of Plant Nutrition.

It is now somewhat generally agreed that formaldehyde constitutes one of the early steps in the photosynthetic process whereby carbon dioxide and water are converted into carbohydrates and oxygen. The difficulty is to isolate the formaldehyde amid the many other substances present in the green leaf. T. Curtius and H. Franzen[22] distilled large quantities of green hornbeam leaves with water, and were able to identify very small amounts of formaldehyde in the distillate. Other green leaves when distilled also gave positive results. They were able to isolate Δ^{α}-hexenaldehyde from the distillate. The presence of this substance must also be connected with carbon dioxide assimilation, because it was not obtained from the same leaves if they had been kept protected from the light for some time before gathering and distillation.

I. Pouget and D. Chouchak[23] have repeated some of the earlier water-culture experiments on the effect of the concentration of the nutrient solution on the growth of the plant. For each of the critical constituents, nitrate, phosphate, and potash, they found that at very low dilutions (for example, 0·1 milligram of P_2O_5 per litre) the plant gives out, and does not absorb, the constituent. As the concentration increases the absorption increases *pro rata* until a point is reached when the absorption is exactly proportional to the concentration of the nutrient solution. A further point is reached later when the absorption becomes less than indicated by the increased concentration, because it is then determined by the capacity of the plant to assimilate the material taken in. Other unpublished experiments in England would confirm the main conclusion of the authors that within certain limits the absorption of the nutrient materials and the consequent growth of the plant is proportional to the concentration of the solution, even when presented to the roots in unlimited amounts. These facts afford somewhat cogent arguments against Whitney and Cameron's soil solution theory, according to which the concentration of the soil water in such constituents as phosphoric acid and potash is a matter of no account in the nutrition of the plant, because it can fully supply its requirements from a solution of extreme dilution, far below any that would be formed naturally even in the poorest soils. The method of water culture is, however, full of pitfalls, and experiments require to be repeated in large numbers and interpreted with great caution.

E. Ramann[24] has continued his studies of the migration of food

[22] *Ber.*, 1912, **45**, 1715; *Annalen*, 1912, **390**, 89; *A.*, ii, 797, 978.
[23] *Compt. rend.*, 1912, **154**, 1709; **155**, 303; *A.*, ii, 796, 975.
[24] *Landw. Versuchs. Stat.*, 1912, **76**, 157, 165; *A.*, ii, 378.

substances from the leaves of trees prior to the autumnal fall. He finds that the migration chiefly takes place during the comparatively short period after the leaves have begun to change colour. Then a considerable proportion, in some cases amounting to one-half, of the nitrogen and phosphoric acid are returned to the permanent parts of the tree, calcium compounds and silica taking their place. If the leaves are killed by frost before they have yellowed off and died naturally, the migration process is stopped, and the nitrogen, at any rate, remains in the leaves. The analyses indicate, strangely enough, that in such cases the frozen leaves lose their potash and phosphoric acid in a few hours after thawing, although no rain has taken place, but such a conclusion requires further experimental support.

The question of migration also enters into the practical problem of determining the optimum time at which to cut the hay crop, which has again been taken up by C. Crowther and A. G. Ruston.[25] They cut "seeds" hay on four dates separated by approximately fortnightly intervals, and determined the total weight of the crop, its composition, and digestibility, as far as was possible by laboratory methods. The dry matter and the true protein per acre increased the later the cutting, but the "amides" decreased in percentage and finally in absolute amount. The fibre and pentosans increased both relatively and absolutely; the soluble carbohydrates showed some absolute decrease in the latter two cuttings. The value of the food produced per acre, either for maintenance or production, reached its maximum at the third cutting, and then fell off, but the results would indicate that a fair amount of latitude may be allowed in the date of cutting without causing appreciable loss. It would be desirable to have these results repeated on a larger scale, and accompanied by real digestion experiments.

The effect of traces of various metals on the growth of plants continues to be a subject of considerable investigation, especially in France, where the labours of G. Bertrand and his colleagues have considerably advanced the question, especially in connexion with manganese. Several recent papers[26] deal with the dependence of *Aspergillus niger* on manganese and zinc in the nutrient substratum. The conclusions are somewhat remarkable—that such minute traces of manganese as one in ten thousand million have an appreciable effect in increasing the yield of *Aspergillus*, although great precautions have to be taken to free the materials from manganese in order to realise this result experimentally. Again,

[25] *J. Agric. Sci.*, 1912, **4**, 305.

[26] G. Bertrand, *Compt. rend.*, 1912, **154**, 381, 616; M. Javillier, *ibid.*, 383; *A.*, ii, 377.

in the absence of manganese, the fungus will not give rise to conidia; moreover, minute traces of iron and zinc must also be present before the conidia will form. A minute trace of zinc must also be present in the medium to enable the invertase present in the cells of *Aspergillus niger* to act; in its absence the invertase does not diffuse through the cell wall.

The employment of manganese and other so-called "catalytic" manures on a field scale does not make much headway. T. Pfeiffer and E. Blanck[27] report a number of experiments both in pots and with trial plots in the field. The results are not conclusive, however, only in so far as they indicate that the magnitude of the effect produced by the manganese, if any, is not of practical importance. A. J. Brown and F. P. Worley[28] have continued their investigation into the extremely interesting semi-permeable membrane they discovered enveloping the endosperm of barley. They now find that the rate of absorption of water by the barley seeds at different temperatures is an exponential function of the temperature. This leads to a discussion of the constitution of water that would agree with such a result, from which the authors conclude that only the simple molecules are transmitted by the differential septum and assimilated by the starch within. This conclusion is confirmed by the measurements obtained for the water absorbed from a solution of ethyl acetate, which agree with the results obtained for pure water, except for a possible slight associative effect of the ethyl acetate on the water molecules.

Chemistry of Animal Nutrition.[29]

The most notable example of the effect of certain substances existing in food in minute traces only is afforded by the numerous investigations that have led to the discovery of the source of the disease of malnutrition well known in the East under the name of "beri-beri," which has been shown to be identical with a state of polyneuritis that can be induced artificially in fowls and other animals. Beri-beri is prevalent in rice-eating communities, and various theories have been previously advanced to explain its origin; for example, it has been associated with a fungus attacking rice that is stored and allowed to become mouldy, and, again, it has been attributed to the incomplete nature of the proteins contained in rice. It was noticed that many rice-eating communities, often of the poorest character, were free from the disease, whereas others consuming purchased rice of presumably good quality developed

[27] *Landw. Versuchs. Stat.*, 1912, **77**, 33; *A.*, ii, 476.
[28] *Proc. Roy. Soc.*, 1912, B, **85**, 546; *A.*, ii, 1086.
[29] See also pp. 228 *et seq.*

cases of the disease. The next step was the observation that fowls fed on decorticated or polished rice pine away and contract a disease of polyneuritis similar to and presumably identical with beri-beri.[30] If, however, the fowls are fed on whole rice just as it is threshed, they remain healthy; the same diet, also, will induce recovery from the disease induced by the decorticated material. At this stage several lines of investigation coincide. U. Suzuki, T. Shimamura, and S. Odake[31] proceeded to attack the husk or the polishings removed in the process of preparing rice for market. These investigators satisfied themselves that the substance inhibiting the disease could be extracted from the husks by water or alcohol. Finally, by dealing with the alcoholic extract of the fat-free husks, they were able to prepare an alkaloidal substance containing nitrogen, to which the name of oryzanin has been given. Small quantities of this substance will keep animals free from the disease that follows feeding on materials in which it is lacking; for example, dogs fed on boiled meat and husked rice after three or four weeks completely waste away and die if the diet is persisted in. The addition to the daily ration of 0·3 gram of oryzanin, however, brings about a rapid recovery. The same investigators were able to show that the same substance, or one analogous in its effects, could be isolated from extracts of wheat and barley bran, from bread, from oats, cabbages, and other natural foods. Similar experiments have been reported with wheat bran; the white flour from the interior of the endosperm has in certain cases proved incapable of maintaining growth, although it was thoroughly utilised on the addition of a small quantity of the bran or its extract. To test the applicability of these facts to the nutrition of man on white or on so-called "standard" bread, L. F. Newman, G. W. Robinson, E. T. Halnan, and H. A. D. Neville[32] made experiments on themselves, each trial of one or other bread lasting a week. On the whole, absorption of the nutrients was very uniform; from white bread about $3\frac{1}{2}$ per cent. more protein was absorbed, whilst "standard" bread contained rather more phosphates, which were equally well absorbed. When whole-meal bread containing more of the husk was fed, the absorption both of nitrogen and phosphorus compounds was less. There was no evidence of any effect due to the specific cortex compounds, nor could the usual claims made for "standard" bread be substantiated. Indeed, the differences indicated possess no practical importance except when bread becomes the chief, almost the only, article of diet.

[30] See also L. Bréaudat, *J. Pharm. Chim.*, 1911, [vii], **4**, 447 ; *A.*, ii, 64.

[31] *Biochem. Zeitsch.*, 1912, **43**, 89 ; *A.*, ii, 980.

[32] *J. Hygiene*, 1912, **12**, 119 ; *A.*, ii, 658.

The capacity of a given food to bring about live weight increase must, however, be distinguished from the power of merely maintaining equilibrium without growth, and this, as regards the proteins, is well brought out in several American investigations. For example, E. V. McCollum[33] fed pigs with the so-called incomplete proteins, zein and gelatin. For maintenance purposes, to repair the daily wear and tear of nitrogenous tissue, the pigs could utilise these proteins very effectively, up to 80 per cent. with zein and 60 per cent. with gelatin, but for growth and the formation of additional body tissue they possessed much lower values. The author therefore insists on the distinction between the proteins required for growth and those needed for maintenance only.

The discussion on the utilisation of the various nitrogen compounds can be paralleled by the question of the form in which phosphorus compounds must be present in the food in order to be utilised. Most plants contain organic phosphorus compounds, and the question is whether such substances are necessary to the animal or can be replaced by inorganic phosphates. Experimenting with goats, Fingerling[34] finds that deficiency of organic phosphorus compounds in fodder can be repaired by the addition of calcium and other inorganic phosphates. The matter is of some practical importance in the feeding of milch cows and young stock, certain diets being deficient in ash containing phosphates.

A. D. Hall.

[33] *Amer. J. Physiol.*, 1911, **20**, 215 ; *A.*, ii, 63.
[34] *Biochem. Zeitsch.*, 1912, **39**, 239 ; *A.*, ii, 465.

MINERALOGICAL CHEMISTRY.

The year 1912 has not been productive of any remarkable advances in the field of pure Mineralogy. A number of new minerals have been described, but few of them can be regarded as species of any great interest or importance; and although many analyses of well-known minerals have been published, the majority of these have been made for purposes of identification, and have thrown but little light on vexed questions of mineral composition with the notable exception of the work on tourmaline and nephelite, which we owe to American investigators.

On the other hand, in the domain of theory, speculation has been rife, and we shall have to notice some interesting suggestions as to the possible constitution of the silicates.

In the borderland where Chemistry, Physics, and Mineralogy meet considerable activity has prevailed; thus the investigation of binary mixtures by thermal methods has attracted many workers, and some very important attempts to elucidate mineral formation have been successfully carried out by synthetical methods in the Geophysical Laboratory at Washington.

In the domain of chemical crystallography, Fedoroff has proved that the system of classification at which he has laboured so persistently affords us the means of readily identifying by its crystal form alone, any substance of which measurements have been recorded.

Lastly, we must not omit to call attention to the publication by the German Mineralogical Society of volume II of their useful summary entitled "Fortschritte der Mineralogie, Kristallographie und Petrographie."

We will now proceed to a brief survey of the progress made in these various directions, and will follow in the main the method of treatment adopted in previous years.

General and Physical Chemistry of Minerals.

Silicate Fusions.—There has been an increasing tendency of late to apply thermal methods to the study of many systems other than

those composed of silicates, and this is perhaps the reason why there are this year but few researches in the silicate group which call for special comment. Among the most important of these is an investigation into the mutual relations of the compounds $CaAl_2Si_2O_8$ and $Na_2Al_2Si_2O_8$, carried out in the Geophysical Laboratory at Washington.[1] It has already been shown that the former, anorthite, can readily be synthesised by fusing together calcium carbonate, alumina, and silica. It has now been ascertained that the latter exists in two crystalline forms; one stable at temperatures below 1248° (about) is hexagonal, and may be termed soda-nephelite; the other, or higher temperature form, is anorthic, and is called soda-anorthite or carnegieite.

Both forms can be obtained by fusing together sodium carbonate, alumina, and silica in the proper proportions, care being taken to avoid loss of soda by too vigorous heating, for if this occurs, crystals of corundum appear in the product. Neither of these substances has been found in nature, although they enter into the composition of nephelite and of certain plagioclase felspars. Crystals of soda-nephelite sufficiently large for study were obtained by crystallisation from sodium tungstate. On studying the cooling curves and the products obtained by quenching various mixtures of these compounds after they had been heated to definite temperatures for a sufficient length of time, it was found that soda-nephelite and anorthite form mixed crystals with a maximum content of 35 per cent. of the latter substance, corresponding with the presence of 7 per cent. of lime. Carnegieite, on the other hand, will only take up at the most 5 per cent. of anorthite. As the proportion of anorthite increases the birefringence of the nephelite diminishes, and when 23 per cent. of anorthite has been added the originally negative crystals become isotropic. On further addition of anorthite the crystals become positive.

An investigation into the nature of Portland-cement clinker, involving the study of the ternary system lime–alumina–silica, was referred to last year. In the course of the work evidence was obtained which went to show that $8CaO,Al_2O_3,2SiO_2$, the ternary compound obtained by Jänecke, was really a mixture.[2] The latter, however, states that melts of the above composition show a very sharp arrest on the cooling curve, and that under the microscope thin sections of the product are seen to consist of perfectly uniform crystals with only small enclosures of glass.[3]

A certain number of fusion experiments have also been made on

[1] N. L. Bowen, *Amer. J. Sci.*, 1912, [iv], **33**, 551; *A.*, ii, 774.

[2] G. A. Rankin and F. E. Wright, *Zeitsch. anorg. Chem.*, 1912, **75**, 63; *A.*, ii, 554.

[3] E. Jänecke, *ibid.*, **76**, 357; *A.*, ii, 761.

natural minerals[4]; thus olivine (m. p. 1600°) and diopside (m. p. 1363°) gave a eutectic at 1271° containing 40 mol. per cent. of olivine. Wollastonite and anorthite gave a eutectic containing 30 mol. per cent. anorthite at 1285°. Aegirite and anorthite gave a plagioclase felspar intermediate between andesite and labradorite, together with the original components.

A number of binary mixtures of meta-silicates of calcium, magnesium, iron, and manganese, both natural and artificial, have also been examined, and the optical properties of the solidified melts described in detail.[5] The products include rhombic pyroxenes, diopside, clinoenstatite, wollastonite, and hexagonal calcium silicate. The work of Cooper, Shaw, and Loomis on the binary system silica–lead oxide, established the existence of the compounds $2PbO,SiO_2$ and PbO,SiO_2, and evidence was also obtained by others[6] of the probable existence of $3PbO,2SiO_2$ and $3PbO,SiO_2$. Cooper, Kraus, and Klein[7] have confirmed the presence of the first three compounds in the melts, and have shown that the optical properties of the second and third are identical with those of the minerals alamosite[8] and barysilite respectively.

Sulphide Fusions.—A number of binary systems composed of sulphides have also been subjected to thermal analysis. From the mineralogical point of view the results obtained by F. M. Jaeger and H. S. van Klooster[9] in their study of the thioantimonites and thioarsenites are perhaps the most important. When antimony and sulphur are melted together the only compound produced is Sb_2S_3, corresponding with a maximum on the freezing-point curve at 546°. There are eutectic points at 530° and 519°, corresponding with 61·3 and 55 atomic per cent. of sulphur respectively. Mixtures of Sb_2S_3 and Ag_2S (m. p. 842°) give a freezing-point curve with two maxima corresponding with $3Ag_2S,Sb_2S_3$, pyrargyrite (m. p. 483°), and Ag_2S,Sb_2S_3, miargyrite (m. p. 509°). Eutectics are found at 463°, 455°, and 449° corresponding with 81, 64·5, and 28·2 mol. per cent. of Ag_2S respectively. The minerals bolivianite, stephanite, pyrostilpnite, polybasite, and polyargyrite are not represented in the thermal diagram, and have probably been formed from solution.

The system Ag_2S–As_2S_3 gives similar results, the compounds formed being $3Ag_2S,As_2S_3$, proustite (m. p. 490°), and Ag_2S,As_2S_3 (m. p. 417°). Mixtures of artificial proustite and pyrargyrite form

[4] P. Lebedeff, *Ann. Inst. Polytechn. St. Petersburg*, 1911, I, **15**, 691; *A.*, ii, 919.

[5] G. Zinke, *Jahrb. Min.*, 1911, ii, 117; *A.*, ii, 359.

[6] *Ann. Report*, 1910, 227.

[7] H. C. Cooper, E. H. Kraus, and A. A. Klein, *Amer. Chem. J.*, 1912, **47**, 273; *A.*, ii, 452. See also *Centr. Min.*, 1912, 289; *A.*, ii, 645.

[8] *Ann. Report*, 1909, 221.

[9] *Zeitsch. anorg. Chem.*, 1912, **78**, 245; *A.*, ii, 1169.

an unbroken series of solid solutions, a point of considerable interest in view of the fact that the natural minerals only occur mixed to a very limited extent.

In the case of the system PbS–Sb_2S_3 two compounds can be recognised, $5PbS,4Sb_2S_3$, plagionite, and $2PbS,Sb_2S_3$, jamesonite, but there is no evidence for the formation under these conditions of the minerals zinckenite, warrenite, heretomorphite, semseyite, boulangerite, meneghinite, or geocronite.

Similar investigations have been made of the binary systems Cu_2S–Sb_2S_3, SnS–Sb_2S_3,[10] and PbS–SnS.[11] The former gives rise to two compounds Cu_2S,Sb_2S_3, corresponding with chalcostibite, and $3Cu_2S,Sb_2S_3$, the main constituent of stylotypite. In the case of the second system the compound SnS,Sb_2S_3 is probably formed. The third system gives two series of solid solutions extending from 0 to 8 per cent. SnS, and from 38·7 to 100 per cent. SnS. The existence of a compound, SnS,PbS, although probable, has not been definitely established.

A certain number of systems involving sulphides and other compounds has also been investigated; thus Quercigh[12] has found that Sb_2O_3 and Sb_2S_3 are miscible in all proportions in the molten state. A compound, $5Sb_2S_3,Sb_2O_3$, is formed, which, however, does not melt unchanged, but decomposes at 522° into Sb_2S_3 and a liquid phase. It gives a eutectic with Sb_2O_3, which has the composition of the mineral kermesite, $2Sb_2S_3,Sb_2O_3$. It would appear, therefore, that the latter cannot be obtained from fused mixtures of its components. The behaviour of the sulphide–chloride systems of silver,[13] lead, and copper[14] has also been investigated, and it has been shown that the oxides of tin, zinc, lead, and copper, and the sulphides of the three latter metals are appreciably soluble in molten sodium chloride.[15]

Salt Fusions.—A very large number of binary mixtures of haloids has been examined by various workers,[16] but we need not here do more than refer to certain investigations of binary mixtures of sulphates of the alkali metals with those of the alkaline earths,[17]

[10] N. Parravano and P. de Cesaris, *Gazzetta*, 1912, **42**, ii, 189; *A.*, ii, 942; and *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 535; *A.*, ii, 771.

[11] W. Heike, *Metallurgie*, 1912, **9**, 313; *A.*, ii, 763.

[12] *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 415; *A.*, ii, 562.

[13] C. Sandonnini, *ibid.*, 479; *A.*, ii, 759.

[14] W. Truthe, *Zeitsch. anorg. Chem.*, 1912, **76**, 161; *A.*, ii, 763.

[15] H. Houben, *Metallurgie*, 1912, **9**, 592; *A.*, ii, 1056.

[16] Compare C. Sandonnini, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 208, 493; ii, 77; *A.*, ii, 350, 764, 918; M. Amadori, *ibid.*, **21**, i, 467; *A.*, ii, 758; H. Brand, *Centr. Min.*, 1912, 26. See also *Jahrb. Min. Beil.-Bd.*, 1911, **32**, 627; *A.*, ii, 255.

[17] G. Calcagni, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 483; ii, 71, 240, 284; *A.*, ii, 761, 918, 1056.

and to some work on the phosphates of lead.[18] Finally, we may mention that a simple method of studying thermal dissociation has been devised by K. Friedrich,[19] and applied by him to the investigation of the dissociation of the carbonates of lead, zinc, iron, manganese, magnesium, calcium, and barium, including those which occur as minerals.

Constitution of Hydrates and Hydrogels.—G. Tschermak,[20] in continuation of his work on the dehydration of the silicic acids, has measured the velocity of dehydration at constant temperature of a number of hydrated salts. He finds that a well-marked retardation takes place at certain points during dehydration corresponding with the abrupt fall in vapour pressure which accompanies the passage from one stage of hydration to another. Experiments with sodium sulphate, barium chloride, sodium phosphate, and strontium hydroxide gave good results, and even in the case of zeolites similar retardations were observed. The same holds good for hydrogels, retardation taking place at certain definite points, and it would seem that certain hydroxides are to be regarded as containing water of crystallisation at the first retardation point, as, for example, $2Al(OH)_3,H_2O$, whilst others, such as $Si(OH)_4$, decompose, and give lower and more stable states of hydration.

Constitution of the Silicates.—A work of considerable importance devoted to this subject has recently appeared,[21] but it is impossible here to do more than call attention to the nature of the remarkable theory it sets forth.

The silicates are regarded as derived, not from the simple hydroxides $Si(OH)_4$ or $Al(OH)_3$, but from compounds formed by condensation of five or six such molecules to form respectively a pentite or hexite group, linkage taking place through oxygen. These groups may themselves be further linked together to form more complex groupings. By the replacement of hydroxylic hydrogen by metals, and of hydroxyl by fluorine formulæ are obtained for a number of natural silicates. Although it may be felt that the authors go too far when they assign formulæ to certain glasses and to some of the products of the Portland-cement industry, yet their views deserve careful examination on the part of mineralogical chemists.

Some interesting suggestions as to the formulæ of the felspars, leucite, nepheline, the zeolites, and the scapolites, have also

[18] A. V. M. Kroll, *Zeitsch. anorg. Chem.*, 1912, **78**, 95 ; *A.*, ii, 1056.

[19] *Centr. Min.*, 1912, 174, 207, 616, 651, 684.

[20] *Monatsh.*, 1912, **33**, 1087 ; *A.*, ii, 1140.

[21] "Die Silicate in chemischer und technischer Beziehung," W. Asch and D. Asch, Berlin, 1911.

been made recently by H. S. Washington.[22] He regards these minerals as derived from two alumino-silicic acids, the first four being obtained from the acid $H_5AlSi_2O_8$, and the last from $H_{10}AlSi_3O_{12}$, the hydrogen of these acids being replaced, not by variable and independent atoms, but by atomic groups, the total valence of which is that of the basic hydrogens.

Heats of Solution of Minerals.—By the aid of a platinum calorimeter the heat evolved when quartz, alumina, and various silicates are dissolved in hydrofluoric acid may be determined.[23] In this way it has been found that the heat of solution of quartz is 29·93 cal. per gram molecule, that of vitreous silica 32·14 cal., and that of alumina 93·86 cal. The heats of formation of certain crystalline silicates have also been calculated, with the following results: adularia, 131·2; leucite, 101·8; microcline, 104·2; analcite, 85·22; natrolite, 95·76; heulandite, 59·44.

Special Properties of Certain Minerals.—The following interesting observations on the solubility in water of calcite and of aragonite are worthy of notice.[24] Solutions were made in silica vessels at temperatures of 25°, 50°, and 100° respectively, with the result that at all three temperatures the solubility of aragonite was found to be slightly greater than that of calcite, the ratio of the solubilities at the several temperatures remaining, however, practically the same. The actual solubilities observed expressed in milligrams per litre are as follows: calcite, 14·33, 15·04, and 17·79; aragonite, 15·28, 16·17, and 19·02.

On determining the solubility of calcium carbonate got by removing carbon dioxide from solutions of calcium hydrogen carbonate at various temperatures, it was found that for the product obtained at 25° the solubility was practically the same as that of calcite. The values for the product obtained at 100° agreed with those of aragonite, whilst the product obtained at 50° gave intermediate results. These observations are in agreement with what is known as to the nature of the crystals which separate from calcium hydrogen carbonate solution at different temperatures.

Some important work has also been done on the behaviour of calcium carbonate when heated under pressure in an atmosphere of carbon dioxide.[25] By means of an apparatus provided with windows of silica glass, and which could be filled with gas under a pressure of 150 atmospheres and heated to 1600°, it was found that pure calcite melts without decomposition at 1289° when heated in carbon dioxide under a pressure of 110 atmospheres. Calcium

[22] *Amer. J. Sci.*, 1912, [iv], **34**, 555.
[23] O. Mulert, *Zeitsch. anorg. Chem.*, 1912, **75**, 198; *A.*, ii, 626.
[24] J. Kendall, *Phil. Mag.*, 1912, [vi], **23**, 958; *A.*, ii, 643.
[25] H. E. Boeke, *Jahrb. Min.*, 1912, **1**, 91; *A.*, ii, 760.

carbonate and lime form a eutectic containing 91 per cent. of the former substance at 1218°, but no mixed crystals or intermediate compounds were observed. The heating curves indicate a change of calcite into another variety at 970°, but the optical character remains unchanged.

In conclusion, we may mention that Meigen's test for calcite and aragonite based on the colours they give when boiled with cobalt nitrate solution has been examined by Niederstadt,[26] and that Vaubel[27] has suggested that the differences in the chemical behaviour of these two minerals may be explained on the assumption that aragonite contains a small quantity of a basic carbonate.

Chemical Crystallography.

The most important matter to be dealt with in this section of our report is the remarkable achievement of Fedoroff,[28] who has brought to a successful issue the stupendous task of reducing to a form available for purposes of reference the chaotic mass of data concerning crystal form collected during the past hundred years.

Since the days of Haüy and Mitscherlich chemists have been well acquainted with the fact that all crystals of the same substance, even if they have been grown under different conditions and possess apparently very different shapes, can always be referred to the same set of crystallographic constants, characteristic of the substance, except in those cases where the difference in form is due to polymorphism, that is, to the existence of two or more distinct varieties of the substance. Again, it has been shown that even in the case of isomorphous substances the angles almost invariably differ by measurable amounts unless they belong to the cubic system.

Now since the crystalline form is a highly characteristic property of a chemical compound, and as, moreover, it has actually been determined in the case of more than 10,000 substances, it would seem reasonable to suppose that the study of crystal form would afford a very valuable means of identification. To a certain limited extent this expectation has been realised, for it has generally been possible to decide, without much difficulty, whether a certain substance A, produced in a chemical reaction, was identical with a known substance B, or not. If, however, it happened that A was proved to be different from B, and the further question was asked "Is A identical with any one of the 10,000 measured substances?" then the inquirer was doomed to disappointment, for until Fedoroff

[26] K. Niederstadt, *Zeitsch. angew. Chem.*, 1912, **25**, 1219; *A.*, ii, 760.
[27] W. Vaubel, *J. pr. Chem.*, 1912, [ii], **86**, 366; *A.*, ii, 1180.
[28] E. S. Fedoroff, *Zeitsch. Kryst. Min.*, 1912, **50**, 513.

undertook the work, no classification of the data existed, and any attempt at comparison was a hopeless task.

The apparently insuperable difficulty which has hitherto stood in the way of any useful employment of the existing data is inherent in the fact that a very large number of compounds crystallise in the orthorhombic, oblique, and anorthic systems. In these systems the values of the crystallographic constants vary enormously with the "setting," that is to say, with the particular faces chosen as prisms, basal plane, and fundamental pyramid. Now the identity of two crystals for which different settings have been adopted can only be established by a highly laborious comparison of angles, and the task may be further complicated by the fact that the habit, that is to say, the particular faces present and their relative development, may often differ greatly if the crystals have been deposited from different solutions.

The first and most important step, then, is to lay down some general principles upon which to decide the choice of the particular setting to be adopted, and thus to insure uniformity of treatment on the part of different crystallographers measuring crystals of the same substance produced in different ways. The great achievement of Fedoroff is that he has succeeded in developing the necessary rules on the sound basis of the theory of crystal structure he has done so much to perfect. Granted, however, that the correct setting has been ascertained, much remains to be done, and here, too, Fedoroff has succeeded in establishing order out of chaos.

In the general case presented by the anorthic system five independent angles are necessary for a complete determination of the form, and of the measured angles the following were selected for tabulation; the angle between the two prism faces, the two angles that these make with the basal plane, the angle from the base on to the most important pyramid plane, and, lastly, the angle of the latter with one of the two prisms. An index was next prepared of the 10,000 substances, arranged according to their systems, and according to the values of the above angles. To identify an unlabelled specimen of any one of these substances is now a fairly easy task. The crystals are measured, preferably, although not necessarily, on a two-circle goniometer, the system is determined, the correct setting ascertained, and the characteristic angles either measured, or calculated from other angles. The index is then searched, the whole process occupying on an average not more than two hours.

The index, although complete, has not as yet been published, but when it becomes available, and crystallographers have mastered the principles which determine the correct setting, it

will no doubt be of immense and ever-increasing value to the chemist. The more, indeed, the chemist and the crystallographer can co-operate, or better, perhaps, be combined in the same person, the greater will be the benefits which may be expected to accrue to the workers in organic chemistry, to whom an easy, but sure and tolerably rapid method of identification is of first-rate importance.

That the classification devised by Fedoroff really does what he claims for it has been demonstrated beyond cavil by the success with which he identified forty-eight out of fifty unlabelled specimens sent to him from this country. Of the remaining two, one had not been previously measured, and therefore was not in his index, and the crystals of the other were not sufficiently developed for complete determination.

It is, of course, obvious that cubic substances, which, after all, are not very numerous, are not amenable to this mode of treatment, nor does it in most cases differentiate between the members of an isomorphous series. In the latter case, however, the type once determined, it is easy to identify the individual by other methods.

Fedoroff's work has been concerned with the co-ordination of existing data, but we have also to chronicle some important contributions to our knowledge of the crystallographic relations of groups of analogous substances; thus the morphology and optical characters of the double chromates of cæsium, rubidium, and ammonium with magnesium chromate have been the subject of exhaustive study,[29] and it has been found that rubidium magnesium chromate and cæsium magnesium chromate exhibit crystal characters precisely similar in their mutual relations to those of the rubidium and cæsium salts of every group of double sulphates and selenates already studied, whilst the position of the ammonium salt in the magnesium group is similar to that found in general for the ammonium salt of any group of double sulphates or selenates of the series.

In the field of organic chemistry, H. E. Armstrong and E. H. Rodd[30] have continued their studies of salts of *p*-dibromobenzenesulphonic acid, and have shown that the lanthanum, neodymium, praseodymium, and cerium salts of this acid crystallise with nine molecules of water in the orthorhombic system, and form a very closely isomorphous series. It will be noticed that the number three plays a very important part in the economy of these salts, for they not only each contain three phenyl groups, three sulphonate groups, and three times three water molecules, but they also possess a

[29] A. E. H. Tutton and Miss M. W. Porter, *Min. Mag.*, 1912, **16**, 169; *A.*, ii, 560.

[30] *Proc. Roy. Soc.*, 1912, A, **87**, 204; *A.*, i, 756.

pseudotrigonal axis. The gadolinium salt with twelve molecules of water is oblique, but also possesses a pseudo-trigonal axis, and the morphology of all five compounds can be correlated with that of *p*-di-iodobenzene. These facts admit of ready explanation on the Pope-Barlow theory of the structure of benzene, the values of the equivalence parameters being exactly what we should expect if the benzene structure is imagined opened out equally in all directions perpendicular to the pseudotrigonal axis to a sufficient extent to admit the insertion of the substituting groups in homogeneous close packing.

Another interesting piece of work has thrown fresh light on the morphotropic relationships which prevail between racemic compounds and their optically active components.[31] Crystalline externally compensated substances may occur either as mechanical mixtures of the dextro- and lævo-forms, as true racemic compounds, or as pseudo-racemic compounds, the crystals of the latter being made up of crystals of the separate optically active forms twinned together. In this last case the form of the compound crystal must of necessity bear a very close relation to those of its components, but it has also been shown that a very close morphotropic relation often exists between the crystals of a true racemic compound and those of its dextro- and lævo-compounds. A particularly striking instance has long been known in the case of sobrerol, and to this may now be added numerous fresh examples, such as racemic camphoric anhydride, benzoyltetrahydroquinaldine, camphoroxime, the hydrogen racemates of potassium, rubidium, cæsium, and ammonium and thallium racemate. On calculating the equivalence parameters in accordance with the Pope-Barlow theory, a very close correspondence is observed between the values obtained for the individual components and for the racemic compound.

The crystallographic relations of a number of salts of *s*-ethanedisulphonic acid have been studied by K. Bleicher.[32] These include salts of ammonium, lithium, sodium, potassium, calcium, strontium, barium, magnesium, zinc, cadmium, and copper. It would appear from the measurements that the nature of the metal is a minor factor in determining the form, and it would therefore be of interest to know the form of the free acid. Unfortunately, however, this could not be obtained in crystals. It was observed that the lithium salts show greater analogies to the salts of the alkaline earths than with the salts of the alkali metals.

This section may be fitly concluded by reference to two important papers of a more theoretical nature. We will begin with an

[31] G. Jerusalem, *T.*, 1912, **101**, 1268.

[32] *Zeitsch. Kryst. Min.*, 1912, **51**, 502.

exhaustive discussion on the part of C. Hlawatsch [33] of the various views which have been held as to the nature of isomorphism. The general outcome of this discussion is as follows: In the first place, it is desirable to consider separately the three conditions usually considered necessary for isomorphism, namely, that two different substances should (1) have similar crystal form, (2) have analogous chemical composition, (3) form homogeneous mixed crystals. In the strictest sense of the word all substances which fulfil the first condition are isomorphous. As, however, the external form is merely the expression of internal structure, we may say that those crystalline substances are isomorphous whose structure is analogous. Since the formation of mixed crystals and parallel growths is conditioned or assisted by analogy of structure, these phenomena afford indications of the existence of isomorphism. Since, moreover, similarity of chemical composition will often result in analogy of structure, it is plain that isomorphous substances will often exhibit close chemical analogy. It is, however, quite possible for substances of very different chemical composition to have the same structure, and in such cases we must be on our guard lest we seek to establish chemical relations where none as a matter of fact exist. The formation of mixed crystals cannot be regarded as an all-sufficient condition for isomorphism, as the number of cases of their formation by substances of very different form is continually increasing.

It would seem possible, however, to classify substances according to their degree of isomorphism on the lines of the following scheme:

(1) The substances exhibit no chemical analogy, but show similarities in certain zones which frequently grow parallel.

(2) The substances show analogies in their angles, but do not exhibit the same cleavages or habit. This may be termed isogonism.

(3) The substances form mixed crystals, but have not analogous structure.

(4) The last case is not to be confused with that presented by isopolymorphous substances when the two modifications possess very different stability.

(5) The substances show like structure expressed, not merely by similarity of form, but by like cleavage, twinning, and habit.

(6) The substances have similar crystal structure, and may form mixed crystals, but do not belong to the same crystal sub-class.

(7) The substances possess similar structure with identical symmetry, and form mixed crystals, but are not chemically analogous.

(8) The substances show chemical analogy in addition to the other characters.

[33] *Zeitsch. Kryst. Min.*, 1912, **51**, 417.

(9) Lastly, they possess chemical analogy, form mixed crystals, have similar structure, and angular relations which are functions of the atomic weights of the interchangeable elements.

It is clear, then, that no small difficulties beset all attempts to give a precise definition of isomorphism. Some of these have also been commented upon by T. V. Barker,[34] who has called attention to a number of cases of what he terms unusual types of isomorphism, where close similarity of form is associated with great divergence of chemical type. As examples may be quoted, the compounds $CuTiF_6,4H_2O$, $CuCbOF_5,4H_2O$, and $CuWO_2F_4,4H_2O$, which are all isomorphous and oblique, or $KClO_4$, $BaSO_4$, and KBF_4, which are isomorphous and orthorhombic, or, again, the well-known case of $CaCO_3$ and $NaNO_3$, which are closely isomorphous and rhombohedral. Barker points out that on the ordinary theory of valency no strict chemical similarity can be demonstrated between the members of the above groups, and the same holds good for many others which he enumerates. If, however, the co-ordination theory of Werner be adopted, analogies at once become evident, as may be seen if the members of the first group of compounds quoted above are written in the following form:

$$[TiF_6]Cu + 4H_2O\,;\ \left[Cb\begin{matrix}O\\F_5\end{matrix}\right]Cu + 4H_2O\,;\ \left[W\begin{matrix}O_2\\F_4\end{matrix}\right]Cu + 4H_2O.$$

In developing his argument, Barker draws attention to the great difficulties which attend the application of the Pope-Barlow theory to these complex inorganic compounds, and points out that the conception of a single valency volume may lead to conclusions which are mutually inconsistent. It is obvious that the views put forward in these two communications may be expected to lead to much further discussion and research.

Artificial Formation of Minerals.

The workers at the geophysical laboratory in Washington have published in detail the results of an elaborate investigation into the conditions of formation and mutual relations of the mineral sulphides of iron.[35] They find that crystals of marcasite can be obtained by the action of hydrogen sulphide on ferric salts or by the action of hydrogen sulphide and sulphur on ferrous salts. Low temperatures and the presence of free acid favour its formation, pure marcasite being produced in a solution containing 1 per cent. of sulphuric acid. Less acid solutions and higher temperatures give mixtures of marcasite and pyrites. The latter mineral is

[34] *T.*, 1912, **101**, 2484.

[35] E. T. Allen, J. L. Crenshaw, J. Johnston, and E. S. Larsen, *Amer. J. Sci.*, 1912, [iv], **33**, 169 ; *A.*, ii, 354.

formed by addition of sulphur from solution to amorphous ferrous sulphide or to pyrrhotite and by the action of soluble polysulphides or thiosulphates on ferrous salts. When heated to 450° marcasite is slowly converted into pyrite with evolution of heat, the change being an irreversible monotropic one.

These observations are in accord with the fact that although pyrite may occur as a primary constituent of magmas, marcasite is not so formed. Pyrite occurs in deep veins and in the neighbourhood of hot springs, where it is deposited from water more or less alkaline. Marcasite, on the other hand, occurs in surface veins, and was deposited from cold acid solution. On heating, pyrite is converted into pyrrhotite, the change being a reversible one, and taking place about 565°, for it was found that when heated at 550° in hydrogen sulphide pyrrhotite passed into pyrite, whilst the reverse change took place rapidly at 575°. Pyrrhotite is also produced by heating iron with excess of sulphur, and there is strong reason to believe that the composition of pyrrhotite is not constant, the mineral being really a solid solution of sulphur in ferrous sulphide. From observations of the specific volume of synthetical pyrrhotite it is inferred that saturation occurs with 6·5 per cent. of sulphur, a conclusion which agrees with the maximum percentage of sulphur observed in natural pyrrhotite.

Examination of the synthetical crystals of pyrrhotite confirms the view that the substance is dimorphous. One form, α, stable at high temperatures, is orthorhombic, with close approximation to angles of 60° in the prism zone. It is characterised by considerable development of the basal plane, and is usually elongated parallel to the X axis. The form β, stable at low temperatures, is hexagonal, and almost invariably forms cruciform twins. The dominant forms are the prism and a sharp pyramid. Troilite is not to be regarded as a distinct species, but is the end member of the pyrrhotite series; it has not so far been prepared free from iron.

A most interesting study of the transformation and conditions of formation of the sulphides of zinc, cadmium, and mercury has also been undertaken in the Geophysical Laboratory.[36] It has been found that the change of sphalerite (zinc blende) to wurtzite is a reversible one, and takes place about 1020°. The reverse change occurs slowly, and requires sixty-six hours to complete at 800—900°. The density of wurtzite, 4·087, is slightly less than that of sphalerite, 4·090, and the index of refraction of the latter, 2·3688, lies between those of wurtzite, $\omega = 2{\cdot}356$ and $\epsilon = 2{\cdot}378$. Iron sulphide which so frequently occurs in solid solution in natural sphalerite increases

[36] E. T. Allen, J. L. Crenshaw, and H. E. Merwin, *Amer. J. Sci.*, 1912, [iv], 34, 341; *A.*, ii, 1055.

the specific volume, and also the refractive index, but greatly diminishes the inversion point, the effects being proportional to the amount of iron present.

Fair-sized crystals of wurtzite were obtained by sublimation at 1200—1300°, whilst small dodecahedra of sphalerite were got from molten sodium chloride about 800°, and larger dodecahedra and tetrahedra from potassium polysulphide at 350°. From aqueous solutions both forms were deposited in crystals between 200° and 400°. Hydrogen sulphide precipitates both forms from acid solutions at 250°, the production of sphalerite being favoured by raising the temperature, and that of wurtzite by increasing the acid concentration. Cadmium sulphide exists in but one form, which can be got in good crystals identical with those of greenockite by the action of hydrogen sulphide on cadmium vapour. Mercury sulphide, on the other hand, exists in three forms. The first, cinnabar, D 8·176, is the most stable form, and is readily prepared by digesting either of the other forms with a solution of alkali sulphide. The second, meta-cinnabar, D 7·60, is black and cubic, and is precipitated from dilute acid solutions of mercury salts by sodium thiosulphate. The third is a new red form obtained as a fine, crystalline powder from stronger neutral solutions on addition of sodium thiosulphate.

It is worthy of remark that we observe again here what has already been noticed in the case of pyrite, that the unstable forms of the sulphides are deposited from acid solutions and the stable forms from alkaline solutions, although under certain conditions of temperature and concentration they may also be obtained from acid solutions.

New Minerals.

Albanite.—This name has been given to a black, lustrous substance of a resinous aspect found in Albania.[37]

Allcharite.—Three crystals of a mineral resembling antimonite in appearance were found with urbaite at Allchar in Macedonia. Accurate measurements obtained from one of these crystals showed, however, that the angles of this substance were not only different from those of antimonite, but could not be identified with those of any known species.[38] The system is orthorhombic, $a:b:c = 0{\cdot}9284:1:0{\cdot}6080$, and the forms present {010}, {110}, {210}, {011}, {101}, {111}.

Ampangabéite is a hydrated columbo-tantalate containing uranium found at Ampangabé in Madagascar, where it is met with

[37] C. I. Istrati and M. A. Mihailescu, *Chem. Zentr.*, 1912, i, 1587; *A.*, ii, 773.
[38] B. Ježek, *Zeitsch. Kryst. Min.*, 1912, **51**, 275.

in large, brownish-red, elongated, rectangular crystals, which are said to resemble Brögger's åneriödite.[39]

Arduinite.—A zeolitic mineral from Val dei Zuccanti has been analysed by E. Billows,[40] who finds that the composition may be expressed by the formula $H_{16}CaAl_2Na_4Si_8O_{30}$. As the properties of the substance differ somewhat from those of the known zeolites, he believes it to be a new species.

Arsenoferrite.—The dark brown, pseudomorphous crystals similar in habit to iron-pyrites which occur on gneiss at the Binnenthal, Switzerland, have been found on analysis to contain iron and arsenic in the ratio 1 : 2. It seems likely, therefore, that they originally consisted of $FeAs_2$, for which hypothetical mineral the name arsenoferrite is therefore proposed.[41]

Baeumlerite.—A colourless, transparent, and highly deliquescent mineral occurs in thin bands in the rock-salt of the Desdemona salt mine in the Leine valley.[42] The substance possesses three perfect cleavages at right angles to one another or approximately so. It is optically biaxial and negative. The composition is $KCl,CaCl_2$, and according to Zambonini it is therefore probably identical with chlorocalcite, a mineral from Vesuvius described in 1872 by Scacchi, which has the same composition, and was described as crystallised in cubes with cubic cleavage.[43]

Betafite.—This mineral, a hydrated, uraniferous columbotitanate, occurs at Ambolotara, Madagascar. It has already been described as blomstrandite,[44] by A. Lacroix[45] now considers that it should rank as a separate species.

Chrombrugnatellite.—A scaly, micaceous mineral occurs as lilac-coloured, lenticular masses in a bright green serpentine from Dundas, Tasmania,[46] Its composition appears to be:

$$2MgCO_3,5Mg(OH)_2,2Cr(OH)_3,4H_2O,$$

which is somewhat analogous to that of brugnatellite,

$$MgCO_3,5Mg(OH)_2,Fe(OH)_3,4H_2O.$$

Cryptose.—From a discussion of the composition and properties of a felspar from San Bartholomeu, Alcobaça, V. Souza-Brandão[47]

[39] A. Lacroix, *Compt. rend.*, 1912, **154**, 1040; *A.*, ii, 567. See also *Bull. Soc. franç. Min.*, 1912, **35**, 180.

[40] Extract from *Rivista Min.*, 1912, **41**.

[41] H. Baumhauer, *Zeitsch. Kryst. Min.*, 1912, **51**, 143; *A.*, ii, 949.

[42] O. Renner, *Centr. Min.*, 1912, 106; *A.*, ii, 357.

[43] F. Zambonini, *ibid.*, 270; *A.*, ii, 652.

[44] *Ann. Report*, 1911, 255.

[45] *Compt. rend.*, 1912, **154**, 1040; *A.*, ii, 567. See also *Bull. Soc. franç. Min.*, 1912, **35**, 88.

[46] L. Hezner, *Centr. Min.*, 1912, 569; *A.*, ii, 1061.

[47] *Commun. Comm. Serv. Geol. Portugal*, 1910–1911, **8**, 12.

concludes that albite can exist in polysymmetric, oblique crystals, that is to say, in crystals having all the geometrical properties of the oblique system, but composed of microscopic lamellæ twinned according to the albite law. These lamellæ may be so thin as to be indistinct even under the highest powers of the polarising microscope. For this variety which bears to ordinary albite the relation of orthoclase to microcline, he proposes the name cryptose or kryptoklas.

Didymolite.—Greyish-white crystals somewhat resembling kyanite in appearance occur in crystalline limestone on the Tatarka river, Yeniseisk, Siberia.[48] They are oblique ($a:b:c=0{\cdot}6006:1:0{\cdot}2867$; $\beta=106°$), and invariably twinned. Their composition is represented by the formula $2CaO,3Al_2O_3,9SiO_2$.

Hatchite.—Five minute crystals of a lead-grey mineral, probably a sulpharsenite of lead, were found in the Lengenbach quarry in the Binnenthal in 1902. They cannot be identified with any of the numerous minerals already described from that locality, and are therefore regarded as belonging to a new species.[49] They crystallise in the anorthic system with the following constants: $\alpha=116°53\frac{1}{2}'$, $\beta=85°12'$, $\gamma=113°44\frac{1}{2}'$; $a:b:c=0{\cdot}9787:1:1{\cdot}1575$.

Manandonite.—This interesting mineral has been met with in cavities in the pegmatite veins of Antandrokomby, Madagascar, associated with rubellite and quartz. It occurs as white laminæ, or as mamillary crusts of hexagonal plates.[50] It possesses a micaceous cleavage with pearly lustre. A cleavage flake viewed in polarised light exhibits six regular sectors. An acute positive bisectrix emerges perpendicular to the plate, and the optic axial angle in air is about 30°. The composition may be represented by the formula $Si_6O_{53}B_4Al_{14}Li_4H_{24}$. Water is not expelled until the mineral is heated above 120°.

Melnikowite.—A variety of iron sulphide has been described, which is said to have the same composition as pyrite, but is much more easily attacked by acids and other reagents. It is therefore regarded as a labile form of iron disulphide, which differs from pyrite and marcasite, and the name melnikowite is proposed for it.[51]

Palaite.—Crystalline masses of a flesh-coloured mineral occur in the tourmaline mines of Pala, San Diego Co., California. It has resulted from the alteration of lithiophilite, and has the composition $5MnO,2P_2O_5,4H_2O$.[52]

Ponite.—This name has been assigned to a greyish-pink carbonate

[48] A. Meister, *Jahrb. Min.*, 1912, i, 403; *A.*, ii, 950.
[49] R. H. Solly and G. F. H. Smith, *Min. Mag.*, 1912, **16**, 287.
[50] A. Lacroix, *Bull. Soc. franç. Min.*, 1912, **35**, 225.
[51] B. Doss, *Jahrb. Min. Beil.-Bd.*, 1912, **33**, 662.
[52] W. T. Schaller, *J. Washington Acad. Sci.*, 1912, **2**, 143; *A.*, ii, 456.

of the formula $FeCO_3,5MnCO_3$, found in the Borca Valley, Roumania.[53]

Preslite, see *Tsumebite*.

Rivaite.—This new Vesuvian mineral having the formula $(Ca,Na_2)Si_2O_5$, was recently described by F. Zambonini.[54]

Salmonsite.—This name has been assigned to a manganese and iron phosphate found as buff-coloured masses at Pala, California.[55] It appears to have been produced by the alteration of hureaulite,

$$H_2Mn_5(PO_4)_4,4H_2O,$$

and has the formula $Fe_2O_3,9MnO,4P_2O_5,14H_2O$.

Samiresite occurs as fragile octahedra at Samiresy, Madagascar.[56] It is related to blomstrandite and betafite, but differs from the latter in containing more columbium and less titanium. It also contains a considerable quantity of lead (7·25 per cent. PbO) as well as uranium.

Sheridanite.—This mineral is a variety of chlorite approximating to leuchtenbergite. It contains an unusually large percentage of alumina, and a very small amount of iron, the composition being represented with fair accuracy by the formula $H_6Mg_3Al_2Si_2O_{13}$. It occurs in some quantity as a foliated mass of pale silvery-green scales in Sheridan Co., Wyoming.[57]

Sicklerite and *Stewartite*.—These two minerals are alteration products of lithiophilite found at Pala, San Diego Co., California.[58] The former occurs as dark brown cleavage masses of high refractive index (1·74) and moderate birefringence, and has the formula $Fe_2O_3,6MnO,4P_2O_5,3(Li,H)_2O$. The latter, although it occurs in abundance, is so mixed with other minerals, that a pure sample could not be obtained for analysis. It is a hydrated manganese phosphate, and occurs as fine, pleochroic fibres of high birefringence, arranged normally to the cleavage cracks of the lithiophilite.

Tsumebite or *Preslite*.—A crystalline, emerald-green mineral occurs with azurite, zinc carbonate, and dolomite at Tsumeb, Otavi, German South-West Africa. The density of the minute, oblique crystals is 6·13. It is a hydrated phosphate of lead and copper of the composition given below, and was named tsumebite by K. Busz:

PbO.	CuO.	P_2O_5.	H_2O.	Total.
63·77	11·79	12·01	12·33	99·90

These numbers lead to the formula $5(Pb,Cu)O,P_2O_5,8H_2O$, the

[53] V. C. Buțureanu, *Ann. Sci. Univ. Jassy*, 1912, **7**, 183.
[54] *Rend. Accad. Sci. Fis. Mat. Napoli*, 1912, [iii], **18**, 223.
[55] W. T. Schaller, *J. Washington Acad. Sci.*, 1912, **2**, 143; *A.*, ii, 456.
[56] A. Lacroix, *Compt. rend.*, 1912, **154**, 1040; *A.*, ii, 567.
[57] J. E. Wolff, *Amer. J. Sci.*, 1912, [iv], **34**, 475; *A.*, ii, 1181.
[58] W. T. Schaller, *loc. cit.*

ratio of lead to copper being approximately 2 : 1. The same mineral has been described by V. Rosický under the name preslite.[59] His account agrees with that of Busz, except that he believes the crystal system to be orthorhombic instead of oblique.

Voelckerite.—This name has been proposed for a hypothetical oxy-apatite, $3Ca_3(PO_4)_2,CaO$, which is believed to be a constituent of many members of the apatite group.[60]

Vrbaite.—This interesting mineral is a well-defined substance occurring in good crystals in a mixture of earthy realgar and orpiment at the Allchar mine, Macedonia.[61] It is orthorhombic ($a:b:c=0{\cdot}5659:1:0{\cdot}4836$). The habit is either tabular parallel to 010, the cleavage plane, and these crystals show also faces of the forms {100}, {331}, {111}, and {112}, or pyramidal with the form {111} predominating. Small crystals are deep red and translucent, larger ones bluish-black and opaque. The streak is similar to that of proustite. The density is 5·3, and on analysis the substance proved to be a thallous salt of the formula $TlAs_2SbS_5$, derived from the acid HAs_3S_5.

In addition to the above we must here take note of certain other substances which may possibly prove to be new species, but to which so far no names have been assigned. One of these has been observed in minute, blue crystals on sandstone at the mine, Étoile du Congo, Katanga, Congo Free State.[62] The mineral appears to be a hydrated phosphate of copper and cobalt. It is orthorhombic, and the crystals are very similar, both in angles and in optical properties to those of libethenite.

Another substance not as yet fully determined occurs as small nodules in the guano deposits of Réunion.[63] It is soluble in water, and is a hydrated sulphate of ammonium and potassium, possibly the potassium analogue of lecontite, $(Na,NH_4)_2SO_4,2H_2O$.

G. D'Achiardi[64] has recorded the existence of minute crystals of a mineral containing copper and sulphur in the Carrara marble, but its exact nature remains obscure.

Another mineral the characters of which do not seem to agree exactly with those of any known species has been found in minute, green, oblique crystals on copper ore from Atacama.[65] It is suggested that it is a kind of natrochalcite having the formula:

$$CuSO_4,Cu(OH)_2,Na_2SO_4.$$

[59] *Zeitsch. Kryst. Min.*, 1912, **51**, 521.
[60] A. F. Rogers, *Amer. J. Sci.*, 1912, [iv], **33**, 475; *A.*, ii, 565.
[61] B. Ježek, *Zeitsch. Kryst. Min.*, 1912, **51**, 365.
[62] G. Cesàro, *Ann. Soc. Géol. Belg., Publ. rel. au Congo Belge*, 1912, Fasc. II, 41.
[63] A. Lacroix, *Bull. Soc. franç. Min.*, 1912, **35**, 114.
[64] *Proc. verb. Soc. Toscana Sci. Nat.*, 1912, **20**, 54, 77.
[65] P. Walther, *Nature*, 1912, **89**, 322. See *Ann. Report*, 1909, 224.

Mineral Analyses.

Allophane.—Discussion still continues as to the nature of the substances grouped together under this name. The view held by Stremme [66] that they consist of mechanical mixtures of colloidal hydrated alumina and silica being combated by S. J. Thugutt,[67] who points out many differences between the natural minerals and artificial products. He supports his contention by analyses of anauxite and cimolite, which point to the individuality of these species.

Alunogen.—As the result of an investigation of an occurrence of alunogen and halotrichite from New Zealand, J. Uhlig [68] has come to the conclusion that the formula of the former mineral is $Al_2(SO_4)_3,16H_2O$, whilst it is still an open question whether the latter is $FeAl_2S_4O_{16},24H_2O$ or $FeAl_2S_4O_{16},22H_2O$. He points out the special value of refractive index determinations for the identification of these substances.

Amphibole Group.—A number of members of this group have been analysed, and we may call attention to an emerald-green actinolite from Sardinia,[69] to two hornblendes from Central France,[70] which contain but little titanium, and to an amphibole from Hungary [71] exceptionally rich in this element.

Apatite Group.—The analysis of a calcium carbonato-phosphate called dahllite (=podolite) occurring in minute, hexagonal crystals at Tonopah, Nevada, has given occasion for a critical discussion of the published analyses of the apatite group.[72] As a result of this, Rogers concludes that the members of the group are to be regarded as isomorphous mixtures of fluor-apatite, $3Ca_3(PO_4)_2,CaF_2$, chlor-apatite, $3Ca_3(PO_4)_2,CaCl_2$, and carb-apatite, $3Ca_3(PO_4)_2,CaCO_3$, together with a substance not hitherto recognised as entering into the composition of the group, namely, oxy-apatite, $3Ca_3(PO_4)_2,CaO$, for which the name voelckerite is proposed. He also points out that carbon dioxide has been recognised for some time as an essential constituent of apatite, and that $3Ca_3(PO_4)_2,CaCO_3$ actually exists, not only as dahllite, but also as the main constituent of certain ill-defined rock phosphates. He has, moreover, made the

[66] *Ann. Report*, 1911, 253.

[67] *Centr. Min.*, 1912, 35; *A.*, ii, 267. See also Th. A. Nikolaevski, *Bull. Acad. Imp. Sci. St. Pétersbourg*, 1912, [vi], **6**, 715, who proposes the name shangavskite for a hydrated colloidal alumina containing about 41 per cent. of water.

[68] *Ibid.*, 723, 766.

[69] D. Lovisato, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 109; *A.*, ii, 358.

[70] F. Gonnard and P. Barbier, *Bull. Soc. franç. Min.*, 1911, **34**, 228; *A.*, ii, 360.

[71] B. Mauritz, *Föld. Közlöny*, 1910, **40**, 581.

[72] A. F. Rogers, *Amer. J. Sci.*, 1912, [iv], **33**, 475; *A.*, ii, 565.

interesting observation that some varieties of pyromorphite also give indications of the presence of carbon dioxide.

Somewhat similar conclusions have been reached by W. Tschirwinsky,[73] who, in the course of his study of Russian phosphorites, distinguishes the following five groups: (1) fluor-apatites, (2) podolites, (3) those with the composition $2Ca_3(PO_4)_2,CaCO_3,CaF_2$, (4) those with the composition $3Ca_3(PO_4)_2,2CaCO_3$, (5) phosphorites in which the cementing material consists largely of aluminium and iron phosphates.[74]

It is interesting to note that fluor- and chlor-apatites have been synthesised by fusing calcium phosphate with fluorite or calcium chloride respectively, and it has also been shown that the two apatites form a continuous series of mixed crystals.[75]

Awaruite.—Steel-grey, irregular grains of this mineral from the gold-washings on the Pelly River, Yukon, contain 74·34 per cent. of nickel and 21·35 per cent. of iron.[76]

Axinite.—An analysis of hair-brown crystals from Nickel Plate Mountain, British Columbia, has been published by R. A. A. Johnston.[77]

Baddeleyite.—The occurrence of minute crystals and grains of this very rare and interesting mineral, native zirconia, is reported from near Bozeman, Montana, where it is found in a corundum-syenite.[78]

Bastnaesite.—This rare mineral has been met with in Madagascar in cleavage masses somewhat like the zinc-blende from Santander in appearance.[79] The mineral is optically uniaxial, and the smaller of the two indices has been found to be 1·7145 (Na). It is soluble in sulphuric acid with evolution of carbon dioxide and hydrofluoric acid, and on examination with the spectroscope absorption bands due to didymium were seen. A quantitative analysis proved it to be a fluocarbonate of cerium, lanthanum, and didymium similar in composition to the bastnaesite from Cheyenne Mountain, near Pike's Peak. The same mineral has also been met with at Welgevonden, S. Africa, in hexagonal prisms.[80]

Bauxite.—The composition of a number of bauxites especially from Croatia has been determined by M. Kišpatič, who has likewise discussed the mode of origin of the substance and the accessory

[73] *Jahrb. Min.*, 1911, ii, 51; *A.*, ii, 173.
[74] For analyses of a number of other Russian phosphorites, see *A.*, ii, 949.
[75] R. Nacken, *Centr. Min.*, 1912, 545; *A.*, ii, 1061.
[76] R. A. A. Johnston, *Summary Rep. Geol. Surv. Canada*, 1911, 256; *A.*, ii, 358.
[77] *Ibid.*
[78] A. F. Rogers, *Amer. J. Sci.*, 1912, [iv], **33**, 54; *A.*, ii, 172.
[79] A. Lacroix, *Bull. Soc. franç. Min.*, 1912, **35**, 108.
[80] D. P. McDonald, *Trans. Geol. Soc. S. Africa*, 1912, **15**, 74.

minerals it contains.[81] From his observations he has come to the conclusion that bauxite is a residue derived from dissolved limestones and dolomites, and consists for the most part of a colloidal hydrated aluminium oxide, Al_2O_3,H_2O, which he terms sporogelite, together with diaspore, hydrargillite, and certain characteristic accessory minerals. As it is a mixture of variable composition one cannot speak of pure or impure bauxite. E. Dittler and C. Doelter[82] have also occupied themselves with the composition, classification, and nomenclature of bauxite and allied substances. They have declared themselves adherents of the view that bauxite consists of a colloidal aluminium hydrate, and by treating these substances with dyestuffs they distinguish between true bauxite and a mixture of the gel with diaspore, hydrargillite, limonite, and kaolin, thus adopting the position of Cornu, who gave the name kliachite to the isotropic bauxite substance.

Beryl.—From their examination of the beryls of Madagascar, Duparc and his assistants came to the conclusion that two types of this mineral exist. One is of prismatic habit, exhibits few forms, has a relatively low density and indices of refraction, and contains but little alkalis; the other is tabular in habit with a large basal plane; it possesses a higher density and refraction indices than the other type, and contains a considerable quantity of rubidium and cæsium. These conclusions were criticised by Lacroix, who believes that the beryls form a continuous series.[83] In a recent paper, Duparc[84] maintains his original position, and quotes in support of his view two new analyses: (I) of a blue aquamarine from Ambatolampy, and (II) of a green aquamarine from Sahanivotry, both of which belong to his first type. The composition and properties of these beryls are very similar to those of the pink beryl from Tsilaisena, but differ considerably from those of the tabular beryl of Maharitra, which is typical of the second type, and may reasonably be classed as a separate variety under the name vorobyevite proposed by Vernadsky. In reply, Lacroix[85] has reviewed all the ascertained facts as to the properties, especially the density, of beryls from Madagascar, and expresses his conviction that it is impossible to admit the existence of two distinct types of beryl. It is interesting to notice that his views are confirmed by the result of a recent careful study of the composition and properties of three beryls from Elba.[86]

[81] *Jahrb. Min. Beil.-Bd.*, 1912, **34**, 513.
[82] E. Dittler and C. Doelter, *Centr. Min.*, 1912, 19, 104.
[83] *Ann. Report*, 1911, 254.
[84] L. Duparc, M. Wunder, and R. Sabot, *Bull. Soc. franç. Min.*, 1912, **34**, 239; *A.*, ii, 360.
[85] A. Lacroix, *ibid.*, 1912, **35**, 200.
[86] L. Maddalena, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 633; *A.*, ii, 775.

Bismuth.—An interesting occurrence of bismuth is reported from the pegmatite vein of Madagascar, where the element has been found native and as sulphide, both converted for the most part into a basic carbonate.[87]

Clintonite Group.—A specimen of brandisite from Tiriolo (Catanzaro) was found to be unusually rich in magnesia.[88]

Carnotite.—An analysis of a small quantity of this mineral found as a light yellow powder at Mount Pisgah, Pennsylvania, supports the view that the species is a definite one belonging to the uranite group. The formula is $(Ca,K_2)(UO_2)_2(VO_4)_2,xH_2O$, a result in harmony with those of analyses of material from Colorado and South Australia.[89]

Celestite.—A specimen containing 3·2 per cent. of barium sulphate, but no calcium, has been found in limestone near Innsbruck.[90]

Dolomite.—Minute, rhombohedra from the limestone of the Wetterstein, near Innsbruck, were found on analysis to have a somewhat abnormal composition, the results agreeing roughly with the formula $7CaCO_3,4MgCO_3$.[91] A specimen of brown spar from the same district may be represented as $4CaCO_3,4MgCO_3,FeCO_3$.

A white mineral observed as thin seams along the joint-planes of coal proved on analysis to be ankerite.[92] One specimen had nearly the normal composition, $2CaCO_3,Fe(Mn)CO_3,MgCO_3$. An analysis has also been published of a ferriferous dolomite from the Simplon Tunnel.[93]

Epidote.—Good crystals of epidote occur in pegmatite veins traversing granulite at Notodden, Telemark.[94] These have been the subject of a thorough crystallographic and optical study, and both green and red crystals have been analysed. The results lend support to the idea that the red colour of many epidotes is due to the presence of tervalent manganese. A consideration of the series iron epidote–clinozoisite leads to the conclusion that a change in the amount of ferric iron of 0·3 per cent. alters the birefringence to the extent of 0·001.

Felspar Group.—F. Gonnard and P. Barbier[95] have continued their work on French felspars, and have published two analyses of microcline and two of orthoclase, whilst to N. Orloff is due an

[87] A. Lacroix, *Bull. Soc. franç. Min.*, 1912, **35**, 92.
[88] U. Panichi, *Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 518; *A.*, ii, 57.
[89] E. T. Wherry, *Amer. J. Sci.*, 1912, [iv], **33**, 574; *A.*, ii, 774.
[90] A. Haas, *Jahrb. Min.*, 1912, i, 1; *A.*, ii, 564.
[91] *Ibid.*
[92] T. Crook, *Min. Mag.*, 1912, **16**, 219; *A.*, ii, 565.
[93] M. Delgrosso, *Riv. Min.*, 1912, **41**, 56.
[94] O. Andersen, *Archiv Math. og Naturv.*, 1911, **31**, No. 15; *A.*, ii, 1183.
[95] *Bull. Soc. franç. Min.*, 1911, **34**, 235; *A.*, ii, 359.

investigation of a number of anorthoclases from Pyatigorsk, Caucasia[96]; the latter all contain barium, but no strontium. Specimens of labradorite sufficiently pure to repay detailed chemical and physical examination have been described in recent years by Ford and Bradley and by Bonillas[97] respectively. Material very similar to the above has been found in basalt dykes in Co. Down, Ireland.[98] The density of the perfectly fresh transparent crystal fragments is 2·706. The indices of refraction are $\alpha=1{\cdot}5630$, $\beta=1{\cdot}5665$, and $\gamma=1{\cdot}5712$, and the extinctions are $-11°$ on $c(001)$ and $-23°$ on $b(010)$. The composition of the mineral is closely represented by the formula $33NaAlSi_3O_8,5KAlSi_3O_8,62CaAl_2Si_2O_8$.

Fichtelite.—A crystallographic investigation of this curious hydrocarbon, $C_{18}H_{23}$, has shown that the natural crystals from Kolbermoor, near Aibling, have no plane of symmetry, but belong to the hemimorphic class of the oblique system.[99]

Garnet Group.—In the course of an important investigation of the chemical composition of the crystalline schists, cordierite rocks, and sanidinites of the Laacher See region, R. Brauns[1] quotes a number of analyses by J. Uhlig of the included garnets.

Haüyne.—Good crystals of the variety of this mineral termed berzeline, pure enough to repay careful analysis, have been found in peperino near Ariccia.[2] Their composition agrees very closely with that calculated from the formula proposed by Brögger and Bäckström, $(SiO_4)_3Al_2(Al{\cdot}SO_4Na)Na_4$, which may be written in a form analogous to that of the garnet formula.

Ihlëite.—An orange-yellow hydrated iron sulphate found as an efflorescence on graphite at Mugrau, Bohemia, was described by Schrauf in 1877 under the name ihlëite. A very similar substance has recently been observed with iron ores at two localities in the island of Elba.[3] On examination under the microscope the mineral was seen to consist of minute, rhombic or hexagonal plates possessing optical characters in accord with orthorhombic symmetry. On analysis the material from both localities was found, after deducting impurities, to agree with the formula $2Fe_2O_3,5SO_3,16H_2O$. A comparison of the properties of the substance with those of two specimens of copiapite, one from Tierra Amarilla and the other from Copiapo, leads to the conclusion that ihlëite is identical with copiapite, and that the latter mineral is to be regarded as ortho·

[96] *Annuaire Géol. Min. Russie*, 1911, **13**, 21; *A.*, ii, 950.
[97] *Ann. Report*, 1911, 257.
[98] A. Hutchinson and W. C. Smith, *Min. Mag.*, 1912, **16**, 267.
[99] A. Rosati, *Zeitsch. Kryst. Min.*, 1912, **50**, 126.
[1] *Jahrb. Min. Beil.-Bd.*, 1912, **34**, 85.
[2] N. Parravano, *Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 631.
[3] E. Manasse, *Proc. verb. Soc. Toscana Sci. Nat.*, 1911, **20**, 65.

rhombic, and not as oblique as is generally stated.[4] Analyses of the specimens from Tierra Amarilla and from Copiapo confirm the formula given above.

Ilmenite.—The view that ilmenite is to be regarded as FeO,TiO_2, rather than as Fe_2O_3,Ti_2O_3, receives support from analyses of a titaniferous ore from Ekersund, and of an ilmenite crystal from the Urals.[5] Titanium was precipitated by boiling a solution of the potassium hydrogen sulphate melt, iron being first reduced by sulphur dioxide. Total iron was estimated in a solution reduced by sulphur dioxide and ferric iron iodometrically in a hydrochloric acid solution made in absence of air. Confirmatory evidence in favour of this view is found in the fact that whereas compounds containing tervalent titanium evolve hydrogen when treated with alkalis, ilmenite does not. Its behaviour, moreover, towards sulphuric acid is similar to that of a mixture of titanic acid and a ferrous salt.

Iridosmine.—Very small quantities of this mineral have been found in battery concentrates at the New Rietfontein Mines, South Africa.[6] A sample analysed was found to consist of 95·5 per cent. of iridosmine containing about 45 per cent. of iridium. In this connexion attention may be called to a useful summary of all the elements found native compiled by W. Vernadsky.[7]

Kornerupine.—Some crystal fragments, sea-green in colour, and sufficiently transparent to be cut as gem-stones, have recently been described by A. Lacroix from the pegmatites of Madagascar.[8] The density is 3·27, and the refractive indices as follows: $\alpha=1{\cdot}6613$, $\beta=1{\cdot}6733$, $\gamma=1{\cdot}6742$. The composition is represented by the formula $6(Mg,Na_2,K_2,H_2)O,4(Al,Fe)_2O_3,5SiO_2$, which differs somewhat from the formula, MgO,Al_2O_3,SiO_2, usually accepted for the mineral.

Lorandite.—A single crystal of this rare thallium compound, $TlAsS_2$, has been identified on a matrix of iron-pyrites and barytes from the Rambler mine, near Encampment, southern Wyoming.[9]

Lüneburgite.—The results of a new analysis of this mineral may be expressed by the formula $Mg_3(PO_4)_2,1{\cdot}77H_3BO_3,6H_2O$.[10] The dehydration curve shows that $6H_2O$ are lost sharply at 200°, the remainder passing away slowly up to 600°.

Marcasite Group.—The important work on the mineral sulphides

[4] *Ann. Report*, 1907, 298.
[5] W. Manchot and B. Heffner, *Zeitsch. anorg. Chem.*, 1912, **74**, 79; *A.*, ii, 265.
[6] C. B. Horwood, *Trans. Geol. Soc. S. Africa*, 1912, **15**, 51.
[7] *Centr. Min.*, 1912, 758.
[8] *Compt. rend.*, 1912, **155**, 672; *A.*, ii, 1182.
[9] A. F. Rogers, *Amer. J. Sci.*, 1912, [iv], **33**, 105; *A.*, ii, 265.
[10] W. Biltz and E. Marcus, *Zeitsch. anorg. Chem.*, 1912, **77**, 124; *A.*, ii, 1181.

of iron carried out at the Geophysical Laboratory in Washington has been already referred to, and attention must here be called to a lengthy discussion on the part of A. Beutell [11] of the relationships of marcasite, mispickel, and glaucodote. He comes to the conclusion that the composition of mispickel is $FeS_2 + nFeAs_2$; the normal mineral is not, however, to be regarded as an isomorphous mixture of FeS_2 and $FeAs_2$, but as an individual compound, variations of composition being due to admixture of marcasite on the one hand or of labile Fe_2As_4 on the other. Marcasites which contain arsenic are to be regarded as mixtures of marcasite and mispickel. The formula of mispickel is at least $Fe_2S_2As_2$, and its constitution $Fe<\begin{matrix}S\cdot As\\ |\\ S\cdot As\end{matrix}>Fe$. The glaucodotes are not isomorphous mixtures of FeAsS and CoAsS, but mixtures of normal glaucodote, $FeCoS_2As_2$, of constitution similar to that of mispickel, with marcasite, Fe_2As_4, and usually mispickel also. The cobaltites are mixtures of $Co_2S_2As_2$ with $Fe_2S_2As_2$, and usually pyrites, Fe_2S_4, normal cobaltite being represented as $As<\begin{matrix}Co\cdot S\\ Co\cdot S\end{matrix}>As$.

Mica Group.—The composition of a sericite which occurs in green talc-like aggregates in cracks in quartz strings near Tan-y-bwlch, North Wales, approximates very closely to that of a muscovite from Bengal, and conforms to type I of Clarke's formulæ, $Al(SiO_4\cdot R_3)(SiO_4\cdot Al)_2$.[12]

Molybdenite.—Analyses have been published of specimens found in quartz in the Stilo district of Calabria.[13]

Nephelite.—The difficulties which stand in the way of a satisfactory representation of the composition of nephelite were referred to last year,[14] and it was then pointed out that the analyses always show an excess of silica above that required for the formula $NaAlSiO_4$. The view that this excess is present as silica held in solid solution has received confirmation from recent synthetical work,[15] which has demonstrated that when silica, alumina, and sodium carbonate are fused together in the proportions required to form $NaAlSiO_4$, some of the sodium volatilises, but whereas the excess of alumina separates as corundum, no free silica can be detected by the microscope. The mineral can, however, be represented as consisting of mixtures of the three molecules, $NaAlSiO_4$ (soda-nephelite), $KAlSiO_4$ (kaliophilite), and $NaAlSi_3O_8$ (albite).

[11] *Centr. Min.*, 1912, 225, 271, 299; *A.*, ii, 652.

[12] A. Hutchinson and W. C. Smith, *Min. Mag.*, 1912, **16**, 264.

[13] R. Nasini and E. Baschieri, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 692 *A.*, ii, 773.

[14] *Ann. Report*, 1911, 260.

[15] N. L. Bowen, *Amer. J. Sci.*, 1912, [iv], **33**, 49; *A.*, ii, 176.

Analyses[16] of nephelite occurring in intimate association with albite tend to show that the maximum value of the silica ratio is 2·2.

Penninite.—Colourless, transparent, roughly hexagonal plates occur associated with the ophicalcite at Recess, Connemara, Ireland, and have approximately the same composition[17] as the compact variety of penninite known as pseudophite, of which numerous analyses from different localities have from time to time been published.

Pickeringite.—A re-examination of a substance, called picro-allumogene, by Roster in 1876, and to which the formula

$$2MgSO_4,Al_2(SO_4)_3,28H_2O$$

was assigned, has established its identity with pickeringite,

$$MgSO_4,Al_2(SO_4)_3,22H_2O.$$[18]

The latter formula has been confirmed by analyses of specimens from an iron mine in Elba, from crevices in slate near Lehesten, Saxe-Meinigen, and from the alum-shales of Wetzelstein, near Saalfeld.[19]

Plagionite.—An elaborate crystallographic examination of specimens from Oruro, Bolivia, has been made by F. Zambonini. The composition of these crystals agrees closely with that required by the accepted formula $5PbS,4Sb_2S_3$.[20] The results of this investigation have led Zambonini to discuss the relations existing between plagionite, heteromorphite, and semseyite. He traverses the view put forward by Spencer that these minerals form a morphotropic series, and believes rather that they constitute an isomorphous series of mixed crystals, of which the end members are $5PbS,4Sb_2S_3$ and $5PbS,2Sb_2S_3$. He finds support for his conclusions in the synthetical work of Jaeger and van Klooster,[21] who, by the thermal analysis of the binary system $PbS–Sb_2S_3$, have demonstrated the existence of two compounds, $5PbS,4Sb_2S_3$ (plagionite) and $2PbS,Sb_2S_3$ (jamesonite), but have obtained no evidence of the formation of compounds corresponding with zinckenite, warrenite, heteromorphite, semseyite, boulangerite, meneghinite, or geocronite.

Pyrophyllite.—A. Haas[22] has analysed an earthy, dull green to brown mineral found in small quantities in "Muschelkalk," near Innsbruck. In composition it is intermediate between pyrophyllite and gümbelite.

[16] H. W. Foote and W. M. Bradley, *Amer. J. Sci.*, 1912, [iv], **33**, 439; *A.*, ii, 569.

[17] A. Hutchinson and W. C. Smith, *Min. Mag.*, 1912, **16**, 264.

[18] G. D'Achiardi, *Proc. verb. Soc. Toscana. Sci. Nat.*, 1910, **19**, 25; *A.*, ii, 174.

[19] H. Hess von Wichdorff, *Centr. Min.*, 1912, 42; *A.*, ii, 266.

[20] *Rivista Min.*, 1912, **41**, 1.

[21] F. M. Jaeger and H. S. van Klooster, *Zeitsch. anorg. Chem.*, 1912, **78**, 245; *A.*, ii, 1169.

[22] *Jahrb. Min.*, 1912, i, 12; *A.*, ii, 564.

Pyroxene Group.—In the course of a description of the rocks of the Los Archipelago, West Africa, A. Lacroix[23] has noticed a gabbro which contains a monoclinic pyroxene. This mineral contains much magnesium, is almost uniaxial, and belongs to the group of substances described as enstatite-augites by Wahl, and to which Winchell assigned the name of pigeonite. Analyses have also been published of interesting augites from the province of Rome,[24] and from the plateau of Central France[25]; the latter contains a considerable amount of titanium, and may be called titan-augites.

Revdinskite.—An apple-green ferrimagnesian silicate containing 6·2 per cent. of NiO, found in small quantities in a deposit of chrome-ironstone in the Caucasus, has been referred to this species.[26]

Rutile.—The composition and mutual relations of the minerals of the rutile group have been discussed by W. T. Schaller.[27] He includes in this group rutile, cassiterite, mossite, tapiolite, nigrine, iserite, ainalite, ilmenorutile, and strüverite, and from an examination of the published analyses he concludes that all these substances are to be regarded as isomorphous mixtures of two or more of the following compounds: ferrous columbate, $Fe(CbO_3)_2$, ferrous tantalate (tapiolite), $Fe(TaO_3)_2$, ferrous titanate, $Fe(TiO_3)$, titanyl titanate (rutile), $(TiO)(TiO_3)$, stanyl stannate (cassiterite), $(SnO)(SnO_3)$, and ferrous stannate, $Fe(SnO_3)_2$. Small amounts of zinc arsenate, zinc stannate, ferrous arsenate, and manganous tantalate may also be present.

Of the minerals mentioned above as composing the group, only tapiolite, rutile, and cassiterite are to be regarded as distinct species. Mossite is columbium tapiolite. Nigrine and iserite are iron rutile, ainalite is tantalum cassiterite, while strüverite from Piedmont is to be considered a mixture of 29·9 per cent. of ferrous columbate, 27·4 per cent. of ferrous tantalate, 2·6 per cent. of ferrous titanate, and 40·1 per cent. of titanyl titanate.

It has recently been suggested that rutile may owe its colour to vanadium rather than to iron oxide, and the wide distribution of vanadium and chromium in small quantities has been confirmed by the analysis of various rutiles in which V_2O_5 and Cr_2O_3 have been found in quantities ranging up to 0·55 per cent. and 0·39 per cent. respectively.[28]

Salt.—The older salt beds exploited in the Berlepsch mine at

[23] *Bull. Soc. franç. Min.*, 1912, **35**, 26.
[24] N. Parravano, *Atti R. Accad. Lincei*, 1912, **21**, ii, 469; *A.*, ii, 1182.
[25] F. Gonnard and P. Barbier, *Bull. Soc. franç. Min.*, 1911, **34**, 228.
[26] N. Besborodko, *Jahrb. Min. Beil.-Bd.*, 1912, **34**, 783.
[27] *Bull. U.S. Geol. Survey*, 1912, No. 509, 9; *A.*, ii, 773.
[28] T. L. Watson, *J. Washington Acad. Sci.*, 1912, **2**, 431; *A.*, ii, 1179.

Stassfurt have been the object of an elaborate and interesting chemico-mineralogical investigation.[29] Representative samples were taken at various depths in the deposit, and their constituent minerals were isolated and identified, and their relative proportions determined. They include anhydrite, carnallite, kieserite, langbeinite, loewite, salt, sylvite, polyhalite, and vanthoffite. The composition of a specimen of the latter mineral agrees with the formula $3Na_2SO_4,MgSO_4$. A discussion of the conditions of formation of this deposit in the light of van't Hoff's work leads to the conclusion that the temperature could not have been less than 72° when these beds were laid down.

The crystallisation of salt from pure aqueous solutions, from solutions containing carbamide, and from an artificial "sea-water" have been carefully studied by C. Fastert.[30] The principal results of this interesting piece of work are as follows: In pure aqueous solution the faces of a distorted cube grow equally fast. Addition of carbamide increases the solubility of the salt, and, as is well known, gives rise to the combination of cube and octahedron. The relative development of these faces and their velocity of growth depend on the amount of carbamide present. On evaporating an artificial sea-water at 25°, salt crystallises in octahedra within the limits of the upper carnallite region and the bischofite region of van't Hoff. At 83° it crystallises in cubes, except within the bischofite region, where octahedra are obtained. Under these conditions the presence of magnesium chloride is the determining factor for the production of the octahedral form.

Sapphirine.—This mineral is present in small, greenish-black grains associated with rutile in a considerable dyke-like mass consisting largely of ilmenite occurring in anorthosite rocks at St. Urbain, Quebec.[31] Their composition is given under I below. Translucent crystal fragments of the same mineral have also been reported from the pegmatites of Madagascar.[32] They are deep blue in colour, and present a general resemblance to the Greenland specimens, although their density, 3·31, and refractive indices, $\alpha=1{\cdot}7042$, $\beta=1{\cdot}7074$, $\gamma=1{\cdot}7097$, are somewhat less than those of the Greenland mineral. The results of an analysis are given under II. A comparison of the molecular ratios given under I*a* and II*a* will show that in neither case do the results agree well with the commonly accepted formula, $5MgO,6Al_2O_3,2SiO_2$:

[29] O. Riedel, *Zeitsch. Kryst. Min.*, 1912, **50**, 139; *A.*, ii, 265.
[30] *Jahrb. Min. Beil.-Bd.*, 1912, **33**, 265.
[31] C. H. Warren, *Amer. J. Sci.*, 1912, [iv], **33**, 263; *A.*, ii, 360.
[32] A. Lacroix, *Compt. rend.*, 1912, **155**, 762.

	I.	II.		Ia.	IIa.
SiO_2	13·44	14·90		2·00	2·00
Al_2O_3	62·98	62·55		5·54	4·96
MgO	15·28	21·20	}	4·54	4·46
FeO	9·08	1·78	}		

Spodumene.—The behaviour of spodumene on heating, and its relation to the products obtained by fusing together silicates of lithium and of aluminium have been the subject of several investigations.[33] As regards its melting point, it has been pointed out that the true melting point is the temperature at which the substance passes from the anisotropic to the isotropic-amorphous condition. It has been found that in this mineral double refraction disappears in the case of fine powder after heating to 950°. The density which is unaltered by heating to 920° is reduced from 3·147 to 2·370 at 980°, whilst the heating curve shows a marked discontinuity at 950°. All these facts point to the melting point being 950°, a temperature which marks, therefore, the upper limit of formation of the oblique crystals of spodumene. On heating to a temperature of 1010° there seems reason to believe that a further change occurs.[34] In connexion with this work we may note that the thermal study[35] of the binary system composed of the metasilicates of lithium and aluminium has established the existence of two compounds, $2Li_2SiO_3,Al_2(SiO_3)_3$ and $Li_2SiO_3,Al_2(SiO_4)_3$. The latter appears to be very different from spodumene, which gives rise, however, to the same product when fused and cooled slowly.

Strüverite.—Black, lustrous grains from a tin-bearing alluvium on the Sebantun River, Kuala Kangsar district, Perak, have the following composition[36]:

TiO_2.	Ta_2O_5.	Cb_2O_5.	FeO.	MnO.	SnO_2.	SiO_2.	H_2O.	Total.
45·74	35·96	6·90	8·27	trace	2·67	0·20	0·50	100·24

These results support the view that strüverite is an isomorphous mixture of tapiolite, $Fe(Ta,Cb)_2O_6$, in rutile, TiO_2. A mineral which is probably a member of this group has lately been found in Madagascar in large, tetragonal crystals.[37]

Sulphates.—Hydrated sulphates of aluminium, iron, and magnesium have been observed in veins in the Sonnenburg Tunnel of the Brenner Railway.[38] The material appears to consist for the most part of halotrichite and altered epsomite, accompanied by mirabilite, picromerite, and glaserite.

[33] K. Endell and R. Rieke, *Zeitsch. anorg. Chem.*, 1912, **74**, 33 ; *A.*, ii, 266.
[34] A. Brun, *ibid.*, **75**, 68 ; *A.*, ii, 569.
[35] R. Balló and E. Dittler, *ibid.*, **76**, 39 ; *A.*, ii, 758.
[36] T. Crook and S. J. Johnstone, *Min. Mag.*, 1912, **16**, 224 ; *A.*, ii, 566.
[37] A. Lacroix, *Compt. rend.*, 1912, **154**, 1040 ; *A.*, ii, 568.
[38] A. Brunner, *Rivista Min.*, 1911, **40**, 47.

Synchysite.—The identity of synchysite with the fluo-carbonate of cerium metals, parisite, suggested by Palache and Warren,[39] has been confirmed by the study of the optical properties of the two minerals. As, moreover, the density is the same, and partial analyses gave $R_2O_3 = 60{\cdot}95$ and 60·71 per cent., $CaO = 11{\cdot}96$ and 10·70 per cent. for synchysite and parisite respectively, their identity may be regarded as securely established.[40]

Thorianite.—Three specimens of this mineral have recently been analysed. The first from Ceylon[41] contains more uranium oxide (23·5 per cent. U_3O_8) and less thoria (65·4 per cent.) than most of the thorianite previously examined. This may be explained by assuming that the mineral is an isomorphous mixture of uranium and thorium oxides. The results obtained with the second lead the analyst, M. Kobayashi,[42] to the conclusion that two distinct types of thorianite exist, the ratio $ThO_2 : UO_2$ being almost exactly 6 : 1 in the one case and 2 : 1 in the other, the corresponding percentages being $ThO_2 = 78$ and 60, $U_3O_8 = 15$ and 33. The existence of these simple ratios does not support the view that thorianite is to be regarded as an isomorphous mixture of the two oxides. There appears, moreover, to be a certain amount of difference between the crystals of the two varieties, those with blunt edges containing more thorium than those with sharp edges. The third specimen contains 74·2 per cent. of ThO_2 and 14·1 per cent. of UO_2.[43]

Tourmaline.—A very important contribution to our knowledge of this mineral has been made by W. T. Schaller,[44] who has attempted to throw light on some of the difficulties it presents by determining the physical characters (density, axial ratio, and refractive indices), as well as the chemical composition of carefully selected material from the following localities, mostly in California: (1) pink crystals from Elba, (2) red crystals from Mesa Grande, (3) pale green crystals from Mesa Grande, (4) green crystals from Haddam Neck, Connecticut, (5) blue crystals from Pala, (6) black crystals from Ramona, (7) black crystals from Lost Valley.

The most important of his conclusions are: (1) that Penfield and Foote's general formula, $H_{20}B_2Si_4O_{21}$, holds good; (2) there is no reason to suppose that foreign material is held in solid solution in the tourmaline; (3) the amount of alumina varies inversely as the amount of bivalent oxides present; (4) a large number of com-

[39] *Ann. Report*, 1911, 261.

[40] E. Quercigh, *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 581; *A.*, ii, 773.

[41] W. Jakób and S. Tołłoczko, *Bull. Acad. Sci. Cracow*, 1911, A, 558; *A.*, ii, 172.

[42] *Sci. Rep Tôhoku Imp. Univ.*, 1912, i, 201; *A.*, ii, 1181.

[43] S. D. Kusnetzoff, *Bull. Acad. Sci. St. Pétersbourg*, 1912, [vi], 361; *A.*, ii, 456.

[44] *Zeitsch. Kryst. Min.*, 1912, **51**, 321.

ponents, not less than eight, have to be assumed if the mineral is to be represented as an isomorphous mixture; (5) the physical properties vary with the composition, but the data at present available are too meagre to allow of the deduction of exact relationships.

Tridymite.—It has recently been found[45] that tridymite can readily be prepared in the form of minute, hexagonal plates by fusing sodium silicate with three times its weight of sodium phosphate for six hours at 1000°. Another variety of silica, cristobalite, can be obtained by heating silica-glass in a porcelain furnace. When in a fine state of division the different varieties of silica differ little in their behaviour towards sodium carbonate solution, but vary greatly in their solubility in hydrofluoric acid; thus, when heated for an hour with 1 per cent. hydrofluoric acid, the percentages dissolved are as follows: quartz, 5·2; tridymite, 20·3; cristobalite, 25·8; amorphous silica, 52·9.

Tscheffkinite.—A black mineral somewhat resembling euxenite in appearance, but easily fusible before the blowpipe and readily decomposed by acids with gelatinisation, is found in the pegmatites of Madagascar.[46] Two analyses indicate that the mineral is anhydrous and contains large quantities of cerium, lanthanum, didymium, and titanium. It is probably related to tscheffkinite.

Turquoise.—A very interesting occurrence of crystallised turquoise is reported from near Lynch Station, Campbell Co., Virginia, where it is found in minute, anorthic, bright blue crystals, which possess nearly the same habit and angles as crystals of chalcosiderite.[47] An analysis of pure material gave results in harmony with the formula, $6Al(OH)_2,Cu(OH),H_5,(PO_4)_4$, assigned to the mineral by Penfield.

Zeolite Group.—The commonly accepted formula for *analcite* is $Na_2Al_2(SiO_3)_4,2H_2O$, which requires that soda, alumina, silica, and water should be present in the ratio 1 : 1 : 4 : 2. The ratios actually observed agree with this formula so far as soda and alumina are concerned; the silica and water ratios are, however, in most cases considerably too high, although the proportion 2 : 1 is approximately maintained. An attempt to clear up this discrepancy by analyses of carefully selected homogeneous material from various localities, has merely confirmed the results of early observations, the mean value of the ratios for six different specimens, each of which was analysed in duplicate, being as follows[48]:

$$Na_2O : Al_2O_3 : SiO_2 : H_2O = 1 : 1{\cdot}06 : 4{\cdot}36 : 2{\cdot}20.$$

[45] R. Schwarz, *Zeitsch. anorg. Chem.*, 1912, **76**, 422; *A.*, ii, 756.
[46] A. Lacroix, *Compt. rend.*, 1912, **155**, 672; *A.*, ii, 1182.
[47] W. T. Schaller, *Amer. J. Sci.*, 1912, [iv], **33**, 35; *A.*, ii, 173.
[48] W. H. Foote and W. M. Bradley, *ibid.*, 433; *A.*, ii, 568.

The empirical formula must therefore be written in the form $Na_2Al_2(SiO_3)_4,2H_2O + xH_2Si_2O_5$, which may be interpreted to mean that some other molecule, possibly $Na_2Al_2Si_6O_{16},3H_2O$, is present in solid solution, the case being similar to that of nephelite. Excess of silica has also been noticed in an analcite from Vesuvius.[49]

Among other zeolite analyses may be noticed one of *laumontite*[50] from Heimbach, near Oberstein, where the mineral occurs in large white to reddish-white crystals, and three of *phillipsite*[51] from the leucite-basanite of the Eulenberg, near Leitmeritz. The latter are remarkable as showing wide divergences in composition.

Meteorites.

Some interesting speculations on the origin of meteorites, more particularly of those exhibiting chondritic structure, have been made by L. L. Fermor.[52] He believes that the material of such stony meteorites was once part of a garnet eclogite existing at a considerable depth below the surface of some primeval stellar body. The sudden diminution of pressure which took place on the disruption of the body caused the garnet to liquefy with increase of volume, and the subsequent rapid fall in temperature lead to the recrystallisation of the material in radial aggregates of enstatite and olivine, so characteristic of the meteoric chondules. He finds support for this theory in evidence he has collected for the existence at a considerable depth below the terrestrial surface of a zone of rocks rich in garnets.

An important general investigation of an experimental character is that carried out by F. Berwerth and G. Tammann[53] on the natural and artificial "burnt" zone of meteoric iron, and the behaviour of Neumann's lines in heated kamacite. The latter are probably due to twin-lamellæ revealed on etching, and if this view is correct the lines ought to be weakened or disappear altogether when the kamacite is annealed. This has actually been observed to be the case when plates of the Mount Joy meteorite were heated at about 870°. In the case of the Avče meteoric iron, the lines are not visible in the outer layer of granular kamacite, but on going inwards a layer of irregular structure is met with, containing fragments of the lines, which in turn gives place to the normal internal structure. An artificial burnt zone exhibiting similar appearances can be produced by heating to incipient fusion sections of kamacite wrapped in asbestos paper.

[49] S. J. Thugutt, *Centr. Min.*, 1911, 761; *A.*, ii, 176.

[50] V. Dürrfeld, *Zeitsch. Kryst. Min.*, 1912, **50**, 257; *A.*, ii, 359.

[51] J. E. Hibsch and A. Scheit, *Tsch. Min. Mitt.*, 1911, **30**, 459; *A.*, ii, 774. For other analyses of zeolites, see *A.*, ii, 57, 175, 176.

[52] *Asiatic Society of Bengal*, 1912, Sept. 4. Abs. *Nature*, 1912, **90**, 213.

[53] *Zeitsch. anorg. Chem.*, 1912, **75**, 145; *A.*, ii, 652.

The question as to the possible cosmic origin of certain glassy bodies from Oberkaunitz continues to excite interest. Weinschenk, one of the principal upholders of this view, classed them as tektites,[54] and based his opinion partly on the abnormal composition of the objects. It has, however, been pointed out recently[55] that fragments of an old glass vessel, probably of Venetian origin, have approximately the same composition as the Oberkaunitz tektites, and exhibit the same sort of surface markings as the glasses from Kuttenberg described by Weinschenk. It would appear, therefore, that the composition and surface markings of these bodies cannot be regarded as affording evidence of their cosmic origin.

Among individual meteorites we may note the following:

Arabia.—A meteorite reported to have fallen in the El Hejaz region of Arabia in the spring of 1910 has been examined by J. Couyat.[56] It consists essentially of olivine, enstatite, and clinoenstatite, with a small quantity of felspar, troilite, and nickel-iron.

Brittany.—S. Meunier[57] has called attention to two meteorites, both of which fell in Brittany in recent times, but which have not as yet been properly examined. One fell on June 30th, 1903, in the Canton of Rochefort-en-Terre, Morbihan. It consists principally of olivine with a certain amount of pyroxene and minute grains of nickel-iron. Chondrules are very rare.

The other fell on July 4th, 1890, at Saint Germain-du-Puel, Ille-et-Vilaine. The stone weighs 2·74 kilos., and has a very remarkable shape, for when pieced together with a fragment broken off from it before reaching the ground and found 3 kilometres away, it forms a plate 30 cm. long, 15 cm. wide, and only 5 cm. thick. From a study of the surface markings it is, moreover, evident that this plate must have traversed the atmosphere with one of its flat faces foremost! An examination of a thin section shows that this meteorite is rich in chondrules of enstatite dispersed through a groundmass composed of olivine, pyroxene, and grains of nickel-iron.

El Nakhla.—A shower of meteoric stones fell near the village of El Nakhla El Baharia in the Nile delta on June 28th, 1911. The stones, which are coated with a glossy black skin, consist of a friable aggregate of crystalline grains, of which the larger part, about 75 per cent., is diopside, the rest being mainly a brown olivine. In a thin section a certain amount of interstitial matter can be seen between the grains, resolved by the microscope into an aggregate of felspar laths with augite and magnetite. No metallic iron is

[54] *Ann. Report*, 1911, 267.
[55] A. Rzehak, *Centr. Min.*, 1912, 23.
[56] *Compt. rend.*, 1912, **155**, 916; *A.*, ii, 1183.
[57] *Ibid.*, **154**, 1739; *A.*, ii, 776.

present. Three bulk analyses of the meteorite have been made by Prior,[58] Pollard,[59] and Meunier[60] respectively, with concordant results.

Prior and Pollard agree that the composition of the diopside may be approximately represented as $3MgSiO_3,3CaSiO_3,2FeSiO_3$, but whilst the former has shown that the other main constituent is olivine approximating to $2Fe_2SiO_4,Mg_2SiO_4$, the latter has described it as hypersthene. As Prior's identification rests on an analysis of selected grains confirmed by a determination of the optical properties, there can be little doubt as to its correctness.

This meteorite approaches most nearly to the Angrite group, but may be regarded as a new type, for which the name nakhlite is proposed.[61]

Holbrook.—A shower of meteoric stones took place on July 19th, 1912, near Holbrook, in Navajo County, Arizona, and over 14,000 separate individuals ranging in weight from 6665 grams to less than 0·1 gram have been collected. The material consists of enstatite (50—60 per cent.), olivine, diallage, and glass, with small amounts of nickel-iron, pyrrhotite, magnetite, and chromite. Well-marked chondrules of enstatite are present.[62]

Krouki.—A meteorite found near the place of this name in the Government of Minsk, Russia, has been described by Gristchinsky.[63] It is a typical pallasite, and so exceedingly similar to the Braghine meteorite that it seemed probable that it was really a representative of the same fall.[64] There seems, however, to be good reason for believing that it fell quite recently, in 1892 or 1893, and, if so, we have the curious coincidence that two meteorites of similar composition have fallen in the same district at widely separated dates.

Okano.—This meteoritic iron fell in Japan in 1904. Its external appearance has been described by T. Hiki.[65] Another more recent fall has also been recorded from the same country. It took place on July 24th, 1909, and a number of stones were collected. These are composed of olivine and bronzite with small amounts of nickel-iron and troilite. A bulk analysis of the stone has been published by T. Wakimizu.[66]

A. HUTCHINSON.

[58] G. T. Prior, *Min. Mag.*, 1912, **16**, 274.
[59] J. B. Pollard, *Survey Department (Egypt)*, 1912, Paper No. 25.
[60] S. Meunier, *Compt. rend.*, 1911, **153**, 785; *Ann. Report*, 1911, 267.
[61] See also F. Berwerth, *Tsch. Min. Mitt.*, 1912, **31**, 107.
[62] W. M. Foote, *Amer. J. Sci.*, 1912, [iv], **34**, 437; *A.*, ii, 1183
[63] *Ann. Geol. Min. Russ.*, 1911, **13**, 72.
[64] L. L. Ivanoff, *ibid.*, 114.
[65] *Beiträge z. Min. Japan*, 1912, **4**, 142
[66] *Ibid.*, 145.

RADIOACTIVITY.

The Atomic Weight of Radium.

Two new determinations of the atomic weight of radium have been made. In one[1] a much larger quantity of radium was available than in previous determinations, the total weight of purified radium chloride being 1·35 grams. It was observed that a part of this preparation, which had been kept two years in a stoppered quartz tube, had absorbed oxygen, for on heating to 300° in nitrogen no water was evolved, but on fusion in hydrogen chloride it evolved chlorine and water and lost 5 per cent. in weight. The surface of the quartz tube was completely disintegrated by the action of the radiations. Quartz is an unsuitable material to use for the preservation of radium preparations. By fractional crystallisation of the material from aqueous hydrogen chloride, the value of the atomic weight found rose rapidly to 225·95, and did not further increase after numerous further fractionations. The atomic weight was determined by the aid of the methods and apparatus employed by T. W. Richards by finding the ratios $RaCl_2/AgCl$ and $RaCl_2/Ag$. Radium chloride, dried in nitrogen below 200° and fused in a platinum boat in hydrogen chloride at 900°, was the starting point, this compound being rendered less hygroscopic and more stable in air by fusion. The mean value obtained in both series of determinations was 225·95, individual estimations not differing from the mean by more than 0·03. Both in methods of purification and of estimation the work was in the main a repetition of Madame Curie's investigation, in which the value found was 226·34 on the present values for silver and chlorine. The main points of difference were the preliminary fusion of the salt in hydrogen chloride, the precipitation of the solution with silver in the cold, and the correction for the solubility of the silver chloride by the nephelometer. These differences, taken in conjunction with the greater quantity of material employed, no doubt account for the slightly different value obtained, so that the number 226·0 may be taken to represent the atomic weight of radium, within a very narrow margin of error, when purified and estimated by these methods.

[1] O. Hönigschmid, *Monatsh.*, 1912, **33**, 253; *A.*, ii, 523.

In the other determination[2] very small quantities of material, usually between 2 and 3 milligrams of radium bromide, were actually employed, and the determination was carried out on a modified form of Steele and Grant's micro-balance. The final material was prepared by the fractional crystallisation of 330 milligrams of about 70 per cent. radium bromide, derived from Cornish pitchblende, from water and aqueous hydrogen bromide. The method of determination was also new, the bromide being converted into chloride and vice versa by ignition in hydrogen chloride or bromide respectively, which had the advantages that there were no transferences of the material during the whole determination and only gaseous reagents were employed. The result for the atomic weight was 226·36, a number which is almost identical with that of Madame Curie. The result is interesting mainly on account of the methods, both of purification and of estimation employed. On account of the small quantity of the material and the novel method of weighing adopted, it is, however, impossible to compare this result with the others until the errors have been quantitatively evaluated. The single result given, in which a value practically identical with the international figure was obtained for the atomic weight of barium, using as the material 3·5 milligrams of the chloride, is not sufficient to allow of this being done. As is discussed in the following section, fresh determinations of the atomic weight of radium by methods, both of purification and of estimation, differing as much as possible from those followed by Madame Curie, are called for before this constant can be considered completely known.

The International Radium Standard.

The primary object of the International Radium Standards Committee has been fulfilled. A standard containing 21·99 milligrams of radium chloride, prepared by Madame Curie by methods identical with those which she employed in the determination of the atomic weight and sealed up in a thin glass tube, has been accepted as the International Radium Standard, and is now preserved at the Bureau International des poids et mesures, Sèvres, near Paris. A careful comparison, by various γ-ray methods of this preparation, with three others containing respectively 10·11, 31·7, and 40·43 milligrams of radium, prepared by Hönigschmid in the course of his atomic-weight determination, showed that all four preparations agreed with one another within the limits of experimental error, and certainly within 1 part in 300. One of the Austrian prepara-

[2] R. Whytlaw-Gray and Sir William Ramsay, *Proc. Roy. Soc.*, 1912, A, **86**, 270; *A.*, ii, 413.

tions is to be preserved as a secondary standard at Vienna, and in countries requiring them the National Testing Laboratories are to be provided with sub-standards measured against both the International and Vienna standards. The funds necessary for the purchase of the radium, both for the International and for the British sub-standard, have been privately raised in this country, and it is expected that the British standard will shortly be prepared and handed over to the National Physical Laboratory, where regular provision will be made for the official testing of radium preparations.

The results of the comparison made in Paris of Madame Curie's and the Austrian preparations show that, provided a raw material is employed, such as Joachimsthal pitchblende, containing no or only negligible quantity of thorium, independent workers using the same methods can reproduce at will radium standards agreeing with one another and with the accepted International standard. If thorium is present in appreciable quantity in the radioactive mineral, the presence of mesothorium in the radium extracted will, of course, entirely vitiate the results, as it will yield, in addition to the practically constant γ-radiation of the radium, a continuously varying γ-radiation of the same order of penetrating power, due to mesothorium and its products.

The absolute purity of the preparations so obtained is another question. For the present it suffices that the degree of purity is definite and can be reproduced at will, as this is the primary requirement of any standard.

The absolute purity of radium chloride fractionated by crystallisation from barium chloride to a constant chemical equivalent has already been called in question.[3] In the fractional crystallisation of isomorphous salt mixtures, the end product of the process is that of minimum (or maximum) solubility. It is not invariably the case that this minimum solubility is possessed by one of the two pure components; it may belong to mixed crystals possessing a definite composition. If Hönigschmid's value, 225·95, is the true atomic weight of radium, that of lead, calculated from it by deducting five times 3·99, the atomic weight of helium, would be 206·0, and of uranium, by adding three times 3·99, would be 237·92. Whereas, if it be supposed that the mixture of constant composition obtained by fractional crystallisation still contains 1 per cent. of barium chloride, the atomic weight of radium would be 227·0, from which 207·05 and 238·97, numbers more in accord with the accepted values, would be the calculated values for lead and uranium. Since, however, in Madame Curie's final preparations

[3] W. Marckwald, *Physikal. Zeitsch.* 1912, **13**, 732; *A.*, ii, 323.

an addition of 0·6 per cent. of barium chloride notably strengthened the barium lines in the spark spectrum, it is very difficult to believe that preparations prepared by these methods still contain as much as 1 per cent. of barium chloride. The experimental investigation of the point now being made will be awaited with interest. If other salts of radium and barium are fractionally crystallised, as, for example, the bromide, the proportion between the two elements for the product of constant composition should not be the same as for the chloride if mixed crystals of minimum solubility exist.

α-Rays.

Further progress has been made in the exact determination of the ranges of the α-rays, with a view to testing the Geiger-Nuttall relation between the range of the α-ray and the period of the change in which it is expelled.[4] In the uranium–radium series the difficult question as to the character of the very low-range α-rays of uranium itself has been elucidated by a careful comparison by a special method of the range of the α-rays of pure uranium oxide with those of ionium and polonium, under conditions such that the absorption of the rays in the active film was identical in each case. The form of the curves connecting ionisation with range was, as is to be expected for homogeneous α-rays, identical with ionium and polonium, but the uranium curve was different, and could be compounded out of two such curves shifted relatively to one another by 4 mm. of range. This indicates that the two α-particles, known to be expelled from the uranium atom in its first change, differ in range by 4 mm. The separate ranges in air at 15° were determined to be 2·9 and 2·5 cm.[5]

Confirmation of this has been obtained by the redetermination of the proportion of ionisation contributed by the α-rays of radium and uranium respectively from a uranium mineral, in which these elements are in equilibrium.[6] Boltwood's ratio of 45 : 100.[7] is obviously at variance with the fact that the range of, and therefore the ionisation contributed by, the single α-particle of radium is greater than that of either of the α-particles of uranium. The ratio calculated, on the present exact data between range and ionisation, assuming the ranges of the α-rays of uranium to be, as recently found, 2·9 and 2·5 cm., and that of radium to be 3·3 cm., is 58 : 100. The experimental value, obtained by comparing the

[4] *Ann. Report*, 1911, 275.

[5] H. Geiger and J. M. Nuttall, *Phil. Mag.*, 1912, [vi], **23**, 439 ; *A.*, ii, 408.

[6] Stefan Meyer and F. Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, II*a*, 1404.

[7] *Ann. Report*, 1909, 259.

α-rays from films of pure uranium oxide of negligible thickness with those from the equivalent quantity of pure radium, was found to be 57·3 : 100, which at once confirms the direct determination of the ranges, and renders it improbable that uranium emits two α-particles, one of range about one-half that of the other, as had formerly been inferred.[8]

The apparatus employed in the determination of the ranges of the α-rays of uranium, the construction of which involved considerable experimental skill, has been utilised in a much-needed review of the ranges of the α-rays from the products of the thorium and actinium series.[9] The collected final results for all three series are contained in the following table:

Substance.	Ranges in cm. at 0°.	Ranges in cm. at 15°.	Initial velocity $\times 10^9$ cm./sec.
Uranium-*I*	2·37	2·50	1·47
Uranium-*II*	2·75	2·90	1·54
Ionium	2·85	3·00	1·56
Radium	3·13	3·30	1·61
Radium emanation	3·94	4·16	1·74
Radium-*A*	4·50	4·75	1·82
Radium-*C'*	6·57	5·94	2·06
Radium-*F*	3·58	3·77	1·68
Thorium	2·58	2·72	1·51
Radiothorium	3·67	3·87	1·70
Thorium-*X*	4·08	4·30	1·75
Thorium emanation	4·74	5·00	1·85
Thorium-*A*	5·40	5·70	1·93
Thorium-*C*	4·55	4·80	1·82
Thorium-*C'*	8·16	8·60	2·21
Radioactinium	4·36	4·60	1·80
Actinium-*X*	4·17	4·40	1·77
Actinium emanation	5·40	5·70	1·93
Actinium-*A*	6·16	6·50	2·02
Actinium-*C*	5·12	5·40	1·89

The Geiger-Nuttall relation has been considerably strengthened and extended as the result. In all three series the curves obtained by plotting the logarithms of the radioactive constants and of the ranges as ordinates and abscissæ respectively are in each series essentially straight lines of similar slope. For products of similar period the range of the rays of the uranium products are least, that of the actinium products greatest, the thorium products being intermediate. Although the differences between the three series are small, they are undoubtedly of very great interest. Any α-particle is experimentally indistinguishable from any other, so long as the velocities are adjusted to equality, as can quite easily be arranged by causing the swifter first to pass through a suitable thickness of an absorbing medium. All are radiant helium atoms. The law of

[8] *Ann. Report*, 1911, 274.

[9] Geiger and Nuttall, *Phil. Mag.*, 1912, [vi], **24**, 647 ; *A.*, ii, 1022.

retardation of the velocity during passage through an absorbing medium and the law of increase of ionising power with loss of velocity are identical for all α-particles, and are independent of the nature of the parent atoms from which they have originated. The precise initial velocity of expulsion appears to be a function of the period of transformation, which is the same for all the members of one series, but is different for different disintegration series. Hence there must be some peculiarity of atomic structure preserved intact in the successive members throughout a series of disintegrations, pertaining to that particular series, and distinguishing it from other series. If these data are confirmed, they are therefore obviously of prime importance in connexion with the evolution of the elements.

The clear exceptions to the rule are the α-rays of thorium itself and of radioactinium. For the former the great difficulty of preparing the material free from subsequent products and of the determination, on account of the lowness of the range, may account for the discrepancy. For the latter, the range of the α-particles of radioactinium is somewhat longer than that of actinium-*X*, and it is to be expected, therefore, that its period of average life should be less instead of greater. It is possible that one of these two periods, either that of 28·1 days ascribed to radioactinium, or of 15 days ascribed to actinium-*X*, may be in error. Naturally this has focussed attention on these two products, and already a preliminary announcement has been made that radioactinium consists of two successive products, the first having the period of average life of 28·1 days hitherto ascribed to radioactinium, but emitting no, or but little, radiation, and a subsequent product of period about 19 hours, emitting α-, β-, and γ-rays. The method of separation, however, is not stated.[10]

The substances for which the ranges, but not the periods, are known, are uranium-*II*, radium-*C'*, and thorium-*C'*. For the two latter the very short periods indicated by the long ranges of the α-rays are about 10^{-6} and 10^{-11} second respectively, and therefore are quite beyond the present methods of direct determination. The new value for the range of the α-ray of uranium-*I*, 2·5 cm., fits the curve for the series much better than the previous value. The calculated values for the periods of uranium-*II* and ionium are respectively 2×10^6 and 2×10^5 years. If these are correct, there should exist per gram of uranium about 1 milligram of uranium-*II*, a chemically non-separable element of atomic weight 234·5, the presence of which, however, will only affect the accuracy of the atomic-weight estimation of uranium in the third decimal place. The quantity of ionium in minerals should be about eighty times

[10] J. Chadwick and A. S. Russell, *Nature*, 1912, **90**, 403.

greater than the quantity of radium, or 24·6 grams per 1000 kilos. (25 grams per ton) of uranium. In view of this the failure to detect the spectrum of ionium calls for comment (p. 321).

Attempts have been made to find a theoretical basis for the at present empirical relation between range and period.[11] It is clear, however, that it will not be easy to do so. The ranges of the α-rays from any one product are all alike, whereas the actual periods of life of the individual disintegrating atoms are widely different, the mean only of all the values being constant. Yet the relation holds between the range, which is truly a constant for each individual disintegrating atom, and the period, which is only a statistical constant. Any explanation of the rule would undoubtedly throw light on the nature of the process of disintegration itself. In view of the increasing number of far-reaching deductions which depend on the rule, its present purely empirical character must not be lost sight of. The rule explains at once why no α-particles of a very short range, as, for example, 1 cm., have been detected. If it holds generally, the life of the product emitting such a radiation would be so long that the number of rays emitted would be far below the limit of experimental detection, even by the most sensitive methods.

The string electrometer has been successfully employed in place of the usual quadrant type, in the work of counting, by the electrical method, the number of α-particles expelled from a radioactive substance. In conjunction with a photographic arrangement for recording the jerks of the electrometer mirror, great advances in the accuracy and trustworthiness of the method have been made, as many as 1000 α-particles per minute being photographically registered. The method should enable the fundamental constant, Q,[12] the number of atoms disintegrating per gram of radium per second, to be determined to almost any required degree of accuracy. At the same time the apparatus has been improved in sensitiveness and steadiness by the use of carefully purified helium instead of air as the medium ionised, and it is expected that even the individual recoil-atoms, the kinetic energy of which is about fifty times less than that of the α-particle, will ultimately come within its range of detection.[13]

The scattering of the α-particles by collision with the atoms of matter is of two types, which have been distinguished by the terms "single scattering" and "compound scattering." The first applies to the result of the multitude of very small deflections suffered by

[11] H. A. Wilson, *Phil. Mag.* 1912, [vi], **23**, 981 ; *A.*, ii, 617 ; F. Butavand, *Le Radium*, 1912, **9**, 203 ; *A.*, ii, 722 ; R. Swinne, *Physikal. Zeitsch.*, 1912, **13**, 14 ; *A.*, ii, 219.

[12] *Ann. Report*, 1909, 234.

[13] H. Geiger and E. Rutherford, *Phil. Mag.*, 1912, [vi], **24**, 618 ; *A.*, ii, 1021.

all the α-particles in successive encounters, and the second to the occasional and comparatively rare deflections of the α-particle through large angles as the result of single collisions, on which such important theoretical deductions have been based. It has been shown that the scattering, experimentally observed, agrees well with what is to be theoretically expected.[14] The theoretical variation of range due to the varying chances of collision of the individual α-particles with the gas molecules has also been discussed.[15]

Some interesting results have been obtained in the microscopic examination of the tracks of single α-particles from polonium in a photographic film. Under high magnifications up to 1700 diameters the straight tracks are resolved into straight rows of dark points, corresponding with the granules of the emulsion. It is stated that not all the granules in the direct tract of an α-particle are affected, but there seems to be some lack of clearness on this point, and the opposite could certainly be argued from other facts in the paper. If the α-particles before reaching the film are caused first to traverse varying distances of air, the length of the track in the film and the number of affected granules which constitute the track, both decrease in constant proportion to one another and linearly with the distance of air traversed. The range of the α-particle in air can thus be deduced by a new method from a photomicrographic study of the tracks.[16]

A simple method of measuring and of demonstrating to an audience the range of the α-particle by projection has been devised. It depends on the fact that an atmosphere laden with fumes of ammonium chloride and acted on by an electric field clears when ionised. If one of the edges of a rectangular transparent chamber is coated with an α-ray-giving substance, an electric field being maintained between the opposite faces, and the chamber is filled with fumes of ammonium chloride, these clear away rapidly over the region penetrated by the α-rays, leaving a sharp dividing line between the cloud and the cloud-free space.[17]

β- and γ-Rays.

With the complete elucidation of the physical nature of the α-rays, the attention of investigators has largely been transferred to the β-rays, which continue to yield results of the highest theoretical significance. The actual photographs which have been published

[14] H. Geiger, *Proc. Roy. Soc.*, 1912, A, **86**, 236; C. G. Darwin, *Phil. Mag.* 1912, [vi], **23**, 901.

[15] K. F. Herzfeld, *Physikal. Zeitsch.*, 1912, **13**, 547.

[16] W. Michl, *Sitzungsber. K. Akad. Wiss. Wien.*, 1912, **121**, IIa, 1431.

[17] K. Przibram, *ibid.*, 221.

of the "magnetic spectra" of line sources of β-rays, resolved into separate beams by a magnetic field, are full of interest, and reveal the extraordinary complexity of the phenomenon.[18] At least twenty-nine sets of distinct β-radiations have been recognised in the photographs of the rays of radium-*B* and -*C*. The β-rays of uranium-*X* and radium-*E* and the swifter β-rays of mesothorium-2 and of thorium-*C* + -*D* have not yet been resolved, and their magnetic spectra consist of, or contain, broad bands, which may or may not prove to be resolvable into distinct lines by more powerful methods. In the other cases the β-radiation has been resolved and for each product several distinct beams have usually been recognised. In the products of the thorium series thirteen distinct beams and two bands exist. This is in striking contrast to the α-rays. Each α-ray-giving product yields only one type of α-radiation, or, to put it even more explicitly, each disintegrating atom gives one α-particle, the initial velocity of which is, within the narrow limits of experimental detection, the same for all the disintegrating atoms of the same kind. Both types of radiation, however, suffer a loss of velocity in passage through matter, which for the β-rays is much greater for the slower than for the faster rays.[19] Passing the radiation through absorbing screens causes the magnetic spectrum to be spread out. Hence these kind of experiments can only be done with preparations of infinitesimal mass as sources of β-rays, such as the active deposits, or the radium emanation enclosed in tubes of minimal thickness, in which the absorption of the radiation in the preparation itself is negligible.

In view of the large number of distinct types of β-rays that exist, the number of β-particles emitted per atom disintegrating is of great interest. The researches so far made, by measuring the negative charge transported by the β-rays from preparations in which the number of atoms disintegrating per second can be evaluated, indicate that most probably only one β-particle is expelled from each disintegrating atom.[20] The number, for example, found both for radium-*B* and for radium-*C* was 1·1, for radium-*E* less than one, and for uranium-*X*, thorium-*D* and actinium-*D*, deduced from previous measurements, 1, 0·8, and 1·4 respectively. In any case it is clear that the number is far less than one for each of the numerous distinct types of β-radiation recognised. Using the Lorentz-Einstein theory for calculating the

[18] J. Danysz, *Le Radium*, 1912, **9**, 1; *A.*, ii, 219. J. Danysz and J. Götz, *ibid.*, 6; *A.*, ii, 220. O. v. Baeyer, O. Hahn, and L. Meitner, *Physikal. Zeitsch.*, 1912, **13**, 264; *A.*, ii, 409. O. v. Baeyer, *ibid.*, 485. E. Rutherford, "Radioactive Substances and their Radiations," Camb. Univ. Press, 1912, p. 253. Fig. 70c.

[19] Baeyer, *loc. cit.*

[20] H. G. J. Moseley, *Proc. Roy. Soc.*, 1912, A, **87**, 230; *A.*, ii, 1024.

kinetic energy of the β-particle at various speeds, the kinetic energies of the numerous successive groups of β-radiation given out by radium-*C* can be well expressed by a relation of the form pE_1+qE_2.[21] The values of E_1 and E_2 are respectively 1·12 and 0·356 ($\times 10^{13}e$ ergs), p and q being integers having values between 0 and 9 and 0 and 2 respectively.

For radium-*B*, the successive groups show a nearly constant difference of energy E_3, which is nearly one-half of E_2 ($0{\cdot}173 \times 10^{13}e$ ergs).

The theory has been advanced that the β-particles from any one disintegrating radio-element are, like the α-particles, initially all the same as regards speed, but that, unlike the α-particles, they suffer, whilst still within the parent atom, successive decrements of energy which is utilised in the production of the γ-rays. The β-rays are known to be very easily deflected after expulsion by collision with the molecules of matter, whereas the α-particles plough their way for the most part straight through them. On this view the γ-rays are regarded as analogous to the characteristic *X*-rays excited in the elements by cathode-rays of above a certain critical velocity. At the time the theory was proposed, these radiations had not been experimentally produced in elements of high atomic weight on account of the difficulty of artificially generating cathode-rays of the necessary velocity. It is to be expected, however, that such characteristic radiations would have a penetrating power closely in accord with that possessed by the known γ-rays, whilst the energy of the cathode-rays necessary to excite them would accord with that possessed by the faster β-rays of the radio-elements. The view adapts itself to the conception of the "Saturnian" atom, in which a very large positive charge is concentrated as a single nucleus at the centre and is surrounded by rings of electrons external to it and rotating in planes. In traversing these external rings of electrons, the ejected β-particle suffers its successive decrements of energy, each of which corresponds with the production of a γ-ray. Thus, in the case of radium-*C*, the emission of the β-particles is accomplished by the production of p γ-rays of one kind and q γ-rays of another kind. These suggestions are, no doubt, to be considered as more or less tentative. If further investigations establish the fact that the decrements of energy of the β-particle occur by definite quanta during its passage through the parent atom, and if though $p+q$ γ-rays are produced, not $p+q$ kinds of γ-rays but two kinds only result, the complexity of the β-rays and the apparent homogeneity of the γ-rays would be accounted for, although the structure of the parent atom pro-

[21] E. Rutherford, *Phil. Mag.*, 1912, [vi], **24**, 453, 893; *A.*, ii, 1024; 1913, ii, 4.

ducing this result would require further elucidation. At first sight, however, the complexity of the β-rays and apparent simplicity of the γ-rays, taken in conjunction with the existence of β-rays of high velocity unaccompanied by γ-rays, to be considered later (p. 313), seems additional evidence in favour of regarding the two kinds of radiation as not necessarily causally connected.

The changes which attend the character of the β-radiation during passage through absorbing materials still occupy investigators. The gradual reduction of velocity in aluminium without, at least, the complete destruction of the homogeneous character of the beam, is well brought out in the photographs of the magnetic spectra of the β-rays of the thorium active deposit after passage through aluminium foil.[22] Screens of different metals retard the rays proportionally to the density of the metal. The same conclusion has been reached in experiments on the absorption of β-rays rendered homogeneous by magnetic sorting.[23] The radiation is at first reduced in velocity, with an increase of the specific ionising power. In consequence, the ionisation is at first increased by passage of the radiation through aluminium foil. Only after 0·04 cm. of foil has been traversed is the ionisation reduced by the absorbing screens. However, in passage through platinum a totally different course is followed. The homogeneity of the beam is completely destroyed, and the ionisation, even when absorbing screens of aluminium are used, now decreases according to the usual exponential law. Probably too little account, in former experiments both with β- and γ-rays, has been taken of the specific action of the absorbing material. Light metals, like aluminium, behave very differently from heavy metals, like platinum and lead.

The γ-rays of radium are so superior in penetrating power to ordinary *X*-rays that it is hardly possible to decide whether or not the two radiations are of the same type. The γ-rays obey the "density law" of absorption much more closely than *X*-rays, but of recent years the recognition of characteristic secondary *X*-radiations has gone far toward explaining the peculiarities exhibited in the absorption of *X*-rays by different substances. The gap between the two types of radiation may be considered to have been definitely bridged by a research in which, in the first place, it has been shown that when the very soft type of γ-rays, such as those produced by radium-*E*, are used for comparison, the absorption phenomena encountered are in no way distinct from those exhibited by *X*-rays. Even more important is the proof that the γ-rays of radium-*E* are capable of exciting the same charac-

[22] O. v. Baeyer, *loc. cit.* J. Danysz, *Compt. rend.*, 1912, **154**, 1502 ; *A.*, ii, 617.
[23] W. Wilson, *Proc. Roy. Soc.*, 1912, A, **87**, 310 ; *A.*, ii, 1023.

teristic radiations as are excited by penetrating X-rays[24] in the elements with atomic weights between silver and neodymium. Undoubtedly, in the course of time, the few anomalies encountered in the absorption of the γ-rays, in which the "density law" is departed from, will be rendered clearer by this conception of the existence of radiations characteristic of the atoms of matter and independent of the character of the exciting radiation, so long as this exceeds a certain minimum of what, in acoustics or optics, would correspond with pitch or frequency, necessary to stimulate the atoms into radiation.

Even α-rays, it would appear, possess the power of exciting this characteristic radiation. The preliminary announcement has been made that an excessively small but detectable amount of γ-radiation is excited when the α-rays of radium-C impinge on matter. The conclusion which follows, that all the radio-elements expelling α-rays must give a small amount of γ-radiation also, is supported by very recent experiments, in which it was found that a very rich preparation of ionium emits some γ-rays, but no detectable β-radiation. Three types of γ-rays were distinguished, with the values of μ/D in aluminium 400, 8·2, and 0·15 $(\text{cm.})^{-1}$. These, it is concluded, are probably characteristic radiations of ionium or thorium in three different series. The value for the middle series, 8·2, corresponds roughly with that found for the "L" series excited in thorium by X-rays.[25]

Further results with β- and γ-rays are more conveniently dealt with in the sections *Multiple Disintegration* and *γ-Ray Methods of Measurement*.

δ-Rays.

The low velocity electrons emitted by surfaces under the impact of α-rays are of general interest, because their formation has been recognised as the analogue in solids of the process which in gases results in ionisation.

Certain conclusions seem gradually to have been placed on a firm basis. The δ-rays appear to be emitted with a velocity following Maxwell's distribution law for gas molecules. No definite upper limit can be assigned to this velocity for the same reason as in the case of the velocity of the gas molecules, but for the δ-rays from a polonium-coated metal plate, velocities corresponding with a fall of potential of as much as from 33 to 43 volts have been recognised. With α-rays from another source bombarding a metal plate, the maximum recognisable velocity of the δ-rays corresponds

[24] J. A. Gray, *Proc. Roy. Soc.*, 1912, A, **87**, 489.
[25] J. Chadwick and A. S. Russell, *Nature*, 1912, **90**, 463.

with 15 to 20 volts, and the most probable velocity with 6 volts. From polished surfaces the electrons can escape under their own initial energy of motion, but with rough surfaces, such as those coated with soot, an electric field is necessary to assist them to escape.[26] Certain conclusions that the δ-rays, when first produced, possessed no definite velocity, their velocity being acquired subsequently to their formation, have now been withdrawn.[27]

It has been proved that *X*-rays behave similarly to α-rays in producing δ-rays, and a detailed investigation has established that it is the secondary β-rays, which *X*-rays generate on impact with solids, which produce the δ-rays. If surfaces struck by *X*-rays are covered with paper, very few β-rays are generated, and the δ-radiation is also suppressed. The δ-rays so generated are in every respect identical with those produced by α-rays. The feature of perhaps the most interest appears to be that the speed of the δ-rays is independent both of the nature and temperature of the metal in which it is generated and of the nature of the exciting radiations, and is to be ascribed to some mechanism common to all ionisation. The incident and emergent δ-particles produced by α-rays in passing through a thin sheet of metal are also alike in all respects.[28]

Evidence has, however, been obtained that the layer of adsorbed gas on the surface plays a certain part in the production of δ-radiation. When such surfaces are exposed to α-rays in a high vacuum, the δ-rays generated diminish notably in quantity with lapse of time. No such "fatigue" is noticed with surfaces from which the film of gas has first been removed.[29] The characteristics of the δ-rays are, however, in no way different in the two cases, and it is impossible, however completely the gas film is removed, completely to prevent the emission of δ-rays. Indeed, the number of δ-rays is only reduced by about 30 per cent., a figure which is within the variation in the number of ions produced by the same α-rays in different gases. As is well known,[30] the curves connecting ionisation and range of α-rays have different forms in different gases, when gases of widely different density are compared. Whereas the analogous δ-ray-range curves[31] have, unexpectedly, the same form when surfaces so different in density as those of aluminium, copper, gold, lead and platinum are compared. The emission of δ-rays is thus not four square in all respects with the

[26] Fr. Hauser, *Physikal. Zeitsch.*, 1912, **13**, 936; *A.*, ii, 1026.
[27] N. Campbell, *Phil. Mag.*, 1912, [vi], **23**, 462; **24**, 527; *A.*, ii, 411, 1027.
[28] N. Campbell, *ibid.*, **23**, 46, 462; **24**, 527, 783; *A.*, ii, 221, 411, 1027, 1121.
[29] Pound, *ibid.*, **23**, 813; **24**, 401; *A.*, ii, 514, 886.
[30] *Ann. Report*, 1907, 312; 1909, 237.
[31] *Ibid.*, 1911, 281.

production of ions. That all is not known is shown by the recent discovery of a new radiation itself completely absorbed by a single aluminium foil, $0{\cdot}64 \times 10^{-4}$ cm. in thickness, corresponding with an air equivalent of only 0·58 cm., which causes the emission of δ-rays from surfaces on which it is incident. It has been suggested that part, if not all, of the δ-rays and of the ionisation produced by ionising radiations is due to the intermediate production of this new radiation.[32] Doubtless it accounts for many of the difficulties experienced in the investigation of the subject (see also *Radioactive Recoil*).

X-Rays.

Space must be allowed for a brief reference to the exciting developments now in progress as a result of the discovery that the *X*-rays are capable of showing up the actual space-lattice of a crystal as theoretically conceived by crystallographers.[33] A plate was cut from a crystal of zinc-blende, parallel to a cube face, and perpendicular to one of the principal cubic crystallographic axes. A narrow beam of *X*-rays was directed perpendicularly through it on to a photographic plate. On development, the plate revealed a number of light spots on a dark background. At the centre was a circular spot 0·5 cm. diameter, surrounded symmetrically by sixteen smaller elliptically-shaped spots, arranged in a square, each side consisting of four spots separated by 0·5 cm., the corners of the square being free from spots. Other fainter systems of spots with similar cubic symmetry, parallel or diagonal with the first, appear. One is inside, and the others are outside and at considerable distances from the main square. These spots were ascribed to an interference diffraction photograph of the space-lattice of the crystal.

The activity which followed the original discovery of the *X*-rays has been revived.[34] It has been shown that the *X*-rays, which, of course, do not obey the ordinary optical laws of reflection, are strongly and regularly reflected in accordance with these laws when they impinge on the cleavage planes of a crystal at nearly grazing incidence. Crystals of rock salt and mica sheets have been used, and it is probable that this type of reflection, from the internal crystal planes, accounts fully for the diffraction patterns of the space-lattice obtained. It is almost certainly not surface reflection,

[32] H. A. Bumstead and A. G. McGougan, *Phil. Mag.*, 1912, [vi], **24**, 462; *A.*, ii, 1026.

[33] M. Laue, W. Friedrich, and P. Knipping, *Sitzungsber. K. Akad. München*, 1912, 303, 363. Compare A. E. H. Tutton, *Nature*, 1912, **90**, 307.

[34] W. H. Bragg, *Nature*, 1912, **90**, 219, 360; W. L. Bragg, *ibid.*, 410; C. G. Barkla and G. H. Martyn, *ibid.*, 435.

although a mica strip only 0·1 mm. thick reflects as strongly as a thick crystal. By bending the mica into an arc, the *X*-rays can be brought to a line focus. These discoveries cannot fail to exert a profound influence on the search for a theory, which shall embrace equally all the properties of light, *X*-rays and γ-rays, and reconcile the conflicting aspects of the wave and corpuscular hypotheses.

The Cloud Method of Rendering the Tracks of Rays Visible.

This interesting new method, described last year,[35] has quite fulfilled the expectations that it would prove to be an exceedingly powerful means of settling some of the most difficult questions as to the connexion between ionising radiations and the ionisation they produce. A fine selection of photographs, comprising the tracks of α- and β-rays, and of the secondary β- and cathode-rays produced by beams of γ- and *X*-rays, has been published, together with full details of the vastly improved methods employed in their production.[36] In the first place, the whole clear conception of the nature of the α-rays, with their almost straight paths, their sharply defined range, the increase of the ionisation as the ray penetrates the gas and is slowed down, the columnar ionisation, the "single" and "compound" scattering, which previous researches have disclosed, is shown to be accurate to the minutest particular in these visible records. Minor new points of great interest also appear. At the "single scattering" which usually characterises the end of the path, whenever the angle of deviation is large, a backward short extension of the new path, or "spur," appears. This is probably due to the atom which has been struck and which causes the sudden abrupt deflection, itself acquiring sufficient energy to ionise for a short distance. At the beginning of the path of an α-ray, when it is possible to see the beginning, as in the α-ray expelled from an atom of emanation, for example, an enlarged head appears. This probably marks the ionisation due to the recoil-atom of radium-*A*, which, also, has been otherwise demonstrated by recent experiments.

Likewise, with regard to the β-rays, the general view as to their ionisation and scattering has been confirmed. It is possible to see on the photographs the single pairs of drops corresponding with individual pairs of ions, and even to count the number produced per cm. of path, with results in fair agreement with existing data. In addition to the regularly spaced pairs, clusters of 20 to 30 drops also appear, which indicate that some of the atoms struck them-

[35] *Ann. Report*, 1911, 275.

[36] C. T. R. Wilson, *Proc. Roy. Soc.*, 1912, A, **87**, 277.

selves liberate cathode-rays possessing energy sufficient to ionise for short distances. The scattering is almost wholly of the cumulative or compound type. Gradual and considerable curvature, rather than abrupt changes of angle, characterise the tracks of β-rays so long as their velocity is high.

The *X*-ray photographs show no trace whatever of direct ionisation apart from the secondary cathode-ray liberated from the atoms of the gas, and thus fully bear out the contention that *X*-rays only ionise indirectly. These cathode-rays are of much lower velocity than the β-rays of radium, and show both kinds of deflection, the gradual or cumulative deviation being much the more important factor in scattering. But abrupt deflections, often through 90° or more, also occur, especially at the end of the path. The cathode-rays start apparently in all directions, and no relation between these directions and that of the primary *X*-ray beam has yet been made out. The appearance of these photographs is that of a mass of interlaced fine threads, no one of which is straight, all being both curved and bent characteristically. On close examination, and with enlarged pictures, the individual drops of the clouds and the dotted appearance of the tracks are clearly seen.

Ionisation.

That ionisation is not fundamentally atomic, but depends to some extent on chemical combination, is recognised as one of the very few points of contact between the new subjects dealt with in this report and the older molecular sciences. Thus sulphur dioxide is a denser gas than hydrogen sulphide and absorbs *X*-radiation of all degrees of penetrating power to a greater extent in consequence, yet the relative ionisation in layers of equal thickness is 1·24 times greater in the latter than in the former. In a mixture of oxygen and hydrogen sulphide the ionisation is 1·17 times greater than in a mixture of hydrogen and sulphur dioxide of the same composition.[37] The variation in the number of ions produced in different gases by α-rays has long been recognised. A recent comparison of the ionisation-range curve in mercury vapour at 330° and 451 mm., with that of air at the same temperature and at a pressure adjusted to make the ranges equal, showed that the ionisation produced in mercury is nearly 40 per cent. greater than in air.[38] Yet in these cases the molecular ionisation has been recognised as mainly, at least, an additive property of the atoms

[37] C. G. Barkla and L. Simons, *Phil. Mag.*, 1912, [vi], **23**, 317; *A.*, ii, 222.
[38] T. S. Taylor, *ibid.*, **24**, 296; *A.*, ii, 888.

of the molecule,[39] and not a constitutive property as in the case of *X*-ray ionisation just cited.

The number of pairs of ions produced by the single α-particle of polonium in air has been estimated to be 164,000, the mean energy absorbed in producing one pair of ions, obtained by dividing the energy of the α-particle by this number, being $5{\cdot}3 \times 10^{-11}$ erg.[40]

The extraordinary results obtained from the study of positive rays in vacuum tubes, in which a host of novel types of molecular aggregations have been recognised,[41] belong properly to the subject of Gas Analysis, and cannot be dealt with in detail. Some interesting conclusions as to the true nature of ionisation are, however, put forward. The atoms in a molecule are probably not oppositely charged. Thus, in a molecule of hydrogen or oxygen, the two atoms are not charged respectively with positive and negative electricity. Each atom is, more probably, electrically neutral, containing equal numbers of opposite atomic charges of electricity. The chemical affinity is conditioned by the disposition of these charges with reference to one another. We may infer from this that a single bond holding two similar atoms in a diatomic molecule is not well represented by the conventional symbol, but it necessarily double, such as might graphically be represented by some such symbol as:

This is of interest because a molecule so constituted would possess one degree of freedom less than that with the conventional single bond.

An important paper dealing with the mathematical theory of ionisation by moving electrified particles can only be mentioned here.[42]

γ-Ray Methods of Measurement.

In dealing with the radio-elements, the proportion of the element in different preparations and therefore the relative atomic weight of the element can be determined exactly by methods for the first time essentially different from those so familiar in the case of ordinary elements. In the case of radium, for example, the atomic weight, in terms of those of the other elements involved, could be obtained with fair accuracy by γ-ray measurements without a single weighing on a number of different compounds, such as the chloride, bromide, carbonate, and so on. γ-Ray measurements

[39] *Ann. Report*, 1907, 314. [40] *Phil. Mag.*, 1912, [vi], **23**, 670; *A.*, ii, 412.
[41] Sir J. J. Thomson, *ibid.*, **24**, 209; *A.*, ii, 885.
[42] *Ibid.*, **23**, 449; *A.*, ii, 410.

would invariably be employed, by preference, because the absorption of γ-rays in the substance itself can readily be arranged to be negligible. Thus, γ-ray measurements and the accuracy that can be attained through them are of considerable interest. At Paris in the comparison of the radium standards two main methods were employed. In one,[43] the radium tube was placed on the centre of a large horizontal circular plate of lead, 1 cm. thick, which formed the upper plate of a condenser, the distance between the plates being only a few centimetres. The upper plate was connected to one pole of a battery of 800 volts, the other pole of the battery being earthed, and the lower plate is connected with the one pair of quadrants of an electrometer, the other pair being earthed. At a given moment an earth connexion of the lower condenser plate is broken, and the ionisation current between the condenser plates is exactly neutralised by the Curie quartz electric balance, in which a weight of several kilograms, held in the hand of the operator, is gradually applied to the pan of the instrument so as to keep the needle of the electrometer as near zero as possible. With practice this apparently difficult operation can be accomplished with marvellous precision. As soon as the full weight is applied, the needle swings away from the zero off the scale, and the time is taken. The weight employed divided by the time gives the relative measure of the strength of the γ-rays. The absolute measure of the ionisation current can, if required, be readily deduced from the constant of the electric balance, and does not involve the capacity of the system.

In the second method[44] a form of optical bench was employed, at one end of which a small, shallow, cylindrical ionisation chamber of lead was mounted with the axis parallel to the bench, the radium preparations being supported in the line of the axis on a light aluminium stand sliding on the bench. The ionisation current due to the γ-rays of radium was balanced against the ionisation current due to a surface of uranium oxide, kept constant during the comparison. Balance was obtained by sliding the radium preparation along the bench. In comparing two radium preparations X and Y, if A and B denote the balance distances respectively, measured to the inside surface of the nearer end of the ionisation cylinder, and l is the length of the cylinder, the ratio of the two preparations $X/Y = B(B+l)/A(A+l)$. This ratio is subject to a very small correction for the different absorption of the γ-rays in the air at the two distances.

The two methods gave concordant results with the various radium

[43] A. Debierne, *Le Radium*, 1912, **9**, 169.

[44] E. Rutherford and J. Chadwick, *Proc. Physical Soc.*, 1912, **24**, 141; *A.*, ii, 520.

standards employed, and the error of measurement was estimated as certainly less than 3 parts in 1000. As an example, the numbers found for the 31·13 and 10·11 milligram Vienna standards by comparison with the Paris standard were, in single determinations, 31·24 and 10·13. In absence of other substances giving γ-rays, the quantity of radium in a sealed tube can now be estimated without opening the tube with at least an accuracy of 0·3 per cent.

The second method has been used to measure the absorption coefficient of γ-rays of radium in gases and light substances.[45] The values of μ/D, where μ is the absorption coefficient and D is the density, for γ-rays after traversing 0·3 cm. of lead are 0·048, 0·051, and 0·047 for air, carbon dioxide, and hydrogen respectively, and for the first two for γ-rays after traversing 1 cm. of lead, 0·046 and 0·047. For air at 0° and 760 mm., the value given for μ is 0·0000624.[46] The "average path" of the γ-ray in air is thus about 150 metres. For a great variety of substances of widely different densities, from that of wood to that of lead, μ/D varies from 0·0401 to 0·0599, and has a minimum value for substances of intermediate density. It is greater both for lighter and heavier substances, the difference being the more pronounced the less penetrating the γ-rays employed, as found previously.

In another research the absorption coefficient of the β-rays of radium in air has been directly measured.[47] For radium preparations sealed in glass test-tubes and for short ranges, 0·6 to 1·6 metres, of air, μ is 0·0033(cm.)$^{-1}$, and for longer ranges, 2 to 5 metres, 0·0045. The value obtained for the γ-rays was, however, less than half that given above. The interesting and possibly important observation was made that, for the β-rays from a bare surface of radium active deposit, the value of μ is about 0·012. This value does not alter with time, when the proportion of radium-*C* to radium-*B* is increasing in the active deposit. This indicates that radium-*C* as well as radium-*B* emits a considerable proportion of very easily absorbed β-rays.

Solutions have been published of some important mathematical problems in the absorption of γ-rays in materials of various form.[48]

Helium and Neon.

In an investigation of the mineral waters of the King's Well, Bath, the interesting observation was made that the proportions

[45] J. Chadwick, *Le Radium*, 1912, **9**, 200; *A.*, ii, 718.

[46] Compare also V. F. Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1911, **120**, II*a*, 1205, where the value found for μ was $4{\cdot}47 \times 10^{-5}$(cm.)$^{-1}$.

[47] A. S. Eve, *Trans., Roy. Soc. Canada*, 1911, **5**, iii, 59; *A.*, ii, 717.

[48] H. Thirring, *Physikal. Zeitsch.*, 1912, **13**, 266. E. v. Schweidler, *ibid.*, 453. L. V. King, *Phil. Mag.*, 1912, [vi], **23**, 242.

of argon, neon, and helium therein differ notably from the atmospheric proportions, and that hydrogen and oxygen are absent. There is 0·78 times as much argon, 188·1 times as much neon, and 72·8 times as much helium as in the same volume of atmospheric air. The water contained $1{\cdot}73 \times 10^{-9}$ curie, and the evolved gas $33{\cdot}65 \times 10^{-9}$ curie of emanation, but only $0{\cdot}14 \times 10^{-9}$ gram of radium was present in the water, per litre.[49]

The absence of oxygen and hydrogen, such as might be expected from the radioactive decomposition of the water, and the great preponderance of neon is taken as indirect evidence that neon is produced by the action of the emanation on the water. Neon in such a quantity, however, is an exceptional constituent of mineral spring gases, whereas radioactivity of the degree of the Bath water and higher is comparatively common.

Neon, together with helium, was found to be present in the gases produced from a solution of thorium nitrate, which had been treated with several quantities of radium emanation. The cold charcoal method of separating the helium and neon was employed, whereas a chemical reagent, such as lithium or calcium, which does not absorb the atmospheric argon, if present, is to be preferred in cases where the origin of a small quantity of neon is at issue. The unabsorbed gases had a volume of 0·485 cu. mm., and the spectrum show both helium and neon brilliantly. It was judged from the appearance of the spectrum that from one-third to one-fourth, that is, about 0·177 cu. mm., consisted of neon. The gases absorbed in the cold charcoal were treated for argon, but hardly any was recovered. The conclusion was arrived at that the air-leakage was insignificant, and that the neon must have been produced by the action of the emanation on the solution.

The conclusion, however, is hardly borne out by the evidence. For it was found that 0·5 c.c. of air, which contains 0·006 cu. mm. (not 0·06, as stated), gave a spectrum "comparable in brilliancy with, but not so brilliant as, that of the neon separated from the gases of the thorium solution," which from spectroscopic examination had been adjudged to contain 0·177 cu. mm. of neon.

In a preliminary communication[50] it is stated that neon has been obtained by bombarding fluorite, prepared by precipitation, washing, and heating to dull redness, with cathode-rays in a tube to which oxygen is admitted as required to maintain the pressure at the value best suited for the production of cathode-rays. The surface turns purple, and silicon fluoride, oxygen, and carbon

[49] Sir William Ramsay, *Chem. News*, 1912, **105**, 133; *A.*, ii, 417; *T.*, 1912, **101**, 1367. J. I. O. Masson and Sir W. Ramsay, *ibid.*, 1370.

[50] Sir William Ramsay, *Nature*, 1912, **89**, 502.

monoxide are expelled. The gases evolved during the first few days were rejected, and the fifth quantity pumped off was examined. After absorption of the condensable gases by cold charcoal, the residue was pure neon, without a trace of helium.

Researches on the proportion of the rare gases in French natural springs show that, with the exception of helium, the other members of the family occur in proportions of the same order as in the atmosphere. The conclusion, with regard to neon, is, however, provisional only, owing to the difficulty of accurately estimating this constituent. The springs of the Côte d'Or contain 10 per cent. of helium in the nitrogen and rare gas fraction, whilst the Source Carnot at Santenay is equally rich, and is estimated to yield 17,845 litres of helium annually.[51] The question arises as to the origin of this helium, for the quantity furnished by the Source Carnot requires for its steady annual production some 70,000 kilos. (about 70 tons) of pure radium, equivalent to some hundreds of millions of kilos. of rich uranium minerals. The same question arises with regard to the natural gas in certain parts of America, several of which are stated to contain over 1 per cent. of helium,[52] which must be evolved in enormous quantities.

Thermo-radioactivity.

With the large quantity of radium chloride of definite purity possessed by the Radium Institute of Vienna, determinations have been made of the heat generated and other constants. Under conditions in which the whole of the α- and β-radiation and an estimated fraction of 18 per cent. of the γ-radiation were absorbed in the calorimeter, the heat generated per hour per gram of radium chloride was 100·66 calories, or per gram of radium, 132·26 calories. These figures refer to radium in equilibrium with its first four short-lived products.[53] The energy of the rest of the γ-rays would increase the figure by an amount, still somewhat indefinite, but probably from 3 to 5 calories per gram of element. The values agree so well with the figures calculated from the known data as regards the kinetic energy and number of the α- and β-particles and of the recoiling atoms, that the very important conclusion is arrived at that no appreciable part of the energy of the radiation escapes transformation into heat. No appreciable part, that is to say, is absorbed in doing any other kind of work than that involved in raising the temperature of the surrounding matter.

A further determination of the heat generated by radium, freed

[51] C. Moureu and A. Lepape, *Compt. rend.*, 1912, **155**, 197 ; *A.*, ii, 843.

[52] *Ann. Report*, 1907, 323.

[53] St. Meyer and V. F. Hess, *Monatsh.*, 1912, **33**, 583 ; *A.* ii, 716.

from all its disintegration products,[54] gave the value 25·2 calories per gram of radium per hour, and, as in this case there is no penetrating radiation, the figure is definite. This leaves 107·1 calories for the heat generated by the emanation, radium-*A*, -*B*, and -*C*, under conditions such that the whole of the α- and β-rays and 18 per cent. of the γ-rays are absorbed. What must be considered as a truly remarkable result is that this figure, 25·2 calories, agrees within 1 per cent. with the value calculated from Joule's equivalent, and the number, mass, and kinetic energy of the α-particles expelled from radium, taking into account the energy of recoil, and assuming that the whole of the kinetic energy suffers transformation into heat.

An independent analysis of the heat in calories generated per hour per gram of radium in equilibrium with its first four products is given in the following table as the result of an exhaustive experimental investigation with the radium emanation and its products, interpreted in the light of the other data applying to these products.[55]

	α-Rays.	β-Rays.	γ-Rays.	Total.
Radium	25·1	—	—	25·1
Emanation.....	28·6	—	—	28·6
Radium-*A*	30·5	—	—	30·5
Radium-*B*+-*C*	39·4	4·7	6·4	50·5
Total	123·6	4·7	6·4	134·7

The heat from a tube containing a given quantity of radium emanation in equilibrium with its products was first measured, the emanation was removed as quickly as possible, and from the change with lapse of time in the amount of heat generated, it was deduced that of the total heat 29, 31, and 40 per cent. respectively came from the emanation, radium-*A* and radium-*B*+-*C*. From the velocities of the various α-rays, the proportion should have been 28·8, 30·9, and 40·3 per cent., but taking into account the fact that probably about 4 per cent. of the total energy is due to β- and γ-rays which come from radium-*B* and -*C* only, the heat generated by radium-*C* appears somewhat less than theory indicates. Whether this small difference is significant remains to be seen. On the assumption that the heat effects are proportional to the ionisation produced by the rays, an attempt was made to estimate the proportion of the total heat due to β- and γ-rays, and from these experiments the figures in the table are deduced. They differ from preceding estimates[56] in the increased proportion ascribed to the β-rays. This is because the measurements were done in the

[54] V. F. Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, IIa, 1419.
[55] E. Rutherford and H. Robinson, *ibid.*, 1491.
[56] *Ann. Report*, 1911, 283.

special glass tubes capable of allowing even the α-rays to escape, whereas in ordinary tubes, even the thinnest, a large proportion of the softer β-radiation is absorbed.

It is estimated that the polonium in equilibrium with 1 gram of radium will generate a further 25·86 calories per hour, the amount produced after one year's accumulation being about 1 calorie per hour. The calculated saturation current (in terms of E.S.U. $\times 10^6$) from a gram of radium, free from products, in the form of an infinitely thin film so that there is no absorption, is 1·28 (when half of the radiation only escapes to produce ionisation), whereas that experimentally found was 1·22. The total saturation current calculated for 1 curie of emanation in vessels of infinite dimensions is 2·75, and for the emanation together with its products of rapid change, 6·10, these figures agreeing closely with the various experimental determinations, extrapolated to correspond with vessels of infinite dimensions from the formula of Duane and Laborde.[57] It is clear that the standards of radium employed in the past by different investigators do not differ very widely from that adopted as the International standard.[58]

A determination of the heat generated by a specimen of orangite, estimated by a radioactive method to contain 36 per cent. of thorium, gave in two series 25·4 and 19·4 ($\times 10^{-5}$ calorie per gram per hour), which is about ten times that found for thorium oxide by other observers, and is greatly in excess of that indicated by radioactive theory. Possibly some chemical change in the material may have caused the result, but until the repetition of the experiments now in progress is complete, discussion may be reserved.[59]

Multiple Disintegration.

Thorium-C *or* -C_1 *and* -C_2.—The most definite case of multiple disintegration at present appears to be that of thorium-*C*. Adopting the view that each mode of a dual disintegration obeys the law of a single radioactive change as though the other mode did not occur, at rates indicated by the radioactive constants λ_1 and λ_2 respectively, the parent substance divides itself so that the fraction $\lambda_1/\lambda_1+\lambda_2$ disintegrates according to the first mode and the fraction $\lambda_2/\lambda_1+\lambda_2$ according to the second. The radiation decays exponentially according to the equation $I=I_o e^{-(\lambda_1+\lambda_2)t}$, independently of whether the rays result in both modes or in one only of the two modes of disintegration.[60]

[57] *Ann. Report*, 1910, 256.

[58] H. Mache and St. Meyer, *Physikal. Zeitsch.*, 1912, **13**, 320; *A.*, ii, 520. St. Meyer and V. F. Hess, *Monatsh.*, 1912, **33**, 583; *A.*, ii, 716.

[59] H. H. Poole, *Phil. Mag.*, 1912, [vi], **23**, 183.

[60] F. Soddy, *ibid.*, 1909, [vi], **18**, 739; *A.*, 1909, ii, 952.

If λ_1 and λ_2 are quantities of the same order, as appears to be the case with thorium-*C*, the process is much easier to follow experimentally than if λ_1 and λ_2 are of widely different value, as appears to be the case with radium-*C*. From the general manner in which the radioactive constants vary widely from member to member and from series to series over an extreme range at present known of $1 : 10^{20}$, it is to be expected that the cases in which λ_1 and λ_2 happen to be similar will be few in comparison with those in which they are widely different. There is little doubt that many of the cases of disintegration at present regarded as simple may prove on closer examination to be multiple, with λ_1 and λ_2 widely different. A single parent element may thus give rise to many end-products varying enormously in relative amount, the ratio λ_1/λ_2 fixing also the ratio of the relative amounts of the two end-products in a dual disintegration.

For every 100 α-particles given by the thorium emanation, 100 are given by thorium-*A*, whilst 35, of range 4·55 cm., and 65 of range 8·16 cm. are given by thorium-*C*, indicating that thorium-*C* undergoes a dual disintegration with $\lambda_1/\lambda_2 = 35/65$.[61] In the case of the α-particles of range 8·16 cm., the period estimated by the Geiger-Nuttall relation is 10^{-11} second.

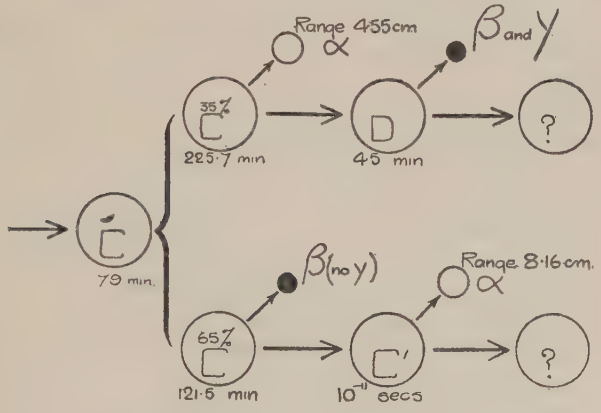
Thorium-*C* disintegrates according to an exponential law with period of average life $1/\lambda = 79$ minutes, so that, on the view taken, $1/\lambda_1 + \lambda_2 = 79$ minutes, and the separate values of λ_1 and λ_2 would be 225·7 and 121·5 minutes. It is these separate periods and not the apparent period which would fix the range of any α-particles emitted in the changes. The first period agrees well enough with the range (4·55 cm.), but it is clear that the longer range α-particle (8·16 cm.) must come from a change with period of the order of 10^{-11} second, and this change must follow the 121·5 minutes period change of thorium-*C*.

In the first place, very numerous attempts to detect any lack of homogeneity in thorium-*C* were unsuccessful. Under all circumstances, the 35/65 ratio between the two sets of α-particles holds good, and this is maintained unaltered as the radiation decays. Thorium-*C*, which had been separated by recoil from the active deposit, by volatilisation at various temperatures and by immersing plates of various electrochemical potentials in the solution of the active deposit, always gives this same ratio. Similarly, when very short exposures to the emanation were given, the active deposit behaved normally, the α-radiation rising to a maximum in two hundred and twenty-five minutes, and maintaining the ratio between the two sets of α-particles unchanged. All this is evidence

[61] T. Barratt, *Proc. Physical Soc.*, 1912, **24**, 112; *A.*, ii, 408.

that thorium-*C* is a homogeneous type of matter, the atoms of which can disintegrate in two distinct ways.[62] Just as, according to present ideas, there is no inherent difference recognisable between atoms of the same radio-element which are about to disintegrate immediately and those which are destined to survive possibly several times the period of average life, the selection following the laws of probability, so in thorium-*C* there seems to be no recognisable difference between those atoms which will expel low-range α-rays (C_1) and those which will expel high-range α-rays (C_2), the laws of probability controlling the number following each mode as though it alone took place.

A most interesting point has, however, transpired. Per atom of thorium-*C* disintegrating one and not two α-particles are expelled, and therefore one β-particle also is expelled.[63] If thorium-*D* were,



Thorium Series.

as previously supposed, the product solely responsible for the β-rays, and if it gave, as in other cases, one β-particle per atom disintegrating, it would follow that thorium-*D* must result from both modes of the disintegration of thorium-*C*. This means that the series after branching must join together again, which is in the highest degree improbable. A closer examination has brought to light the following new facts. All the γ-rays, but only a portion, the relatively smaller portion, of the β-rays, come from thorium-*D*. The greater part of the β-rays, some 65 per cent., come from thorium-*C*, and are unaccompanied by γ-rays. The β-rays expelled by the *C* member are considerably swifter and more penetrating than those expelled

[62] E. Marsden and C. G. Darwin, *Proc. Roy. Soc.*, 1912, A, **87**, 17; *id.*, ii, 823.
[63] *Ann. Report*, 1911, 282.

by the *D*-member. Hence it is reasonably concluded that the disintegration runs as shown in the diagram on p. 313.

The three circles lettered *C* refer to the same substance, disintegrating dually, both modes of disintegration proceeding simultaneously, not successively. The hypothetical, short-lived parent of the 8·16 cm. range α-ray has been designated *C'* for want of a better term. The periods refer to the periods of average life. The facts as regards the β- and γ-rays are well established by entirely independent investigations.[64] The mixed β-rays of thorium-*C* + -*D* are half absorbed in 0·41, of pure -*D* in 0·32, and of pure -*C* (calculated) in 0·48 mm. aluminium. The β-ray curve of pure thorium-*C* rises from an initial value 0·72 to a maximum, reckoned as unity, in ten minutes, whereas the γ-rays rise from an initial value of only 0·05 to a maximum in fourteen to sixteen minutes.

Thus the dual disintegration of thorium-*C* occurs either as an α-ray or a β-ray disintegration. If the α-ray is first expelled, the product gives β- and γ-rays, whereas if the β-ray is first expelled it is unaccompanied by γ-rays, and the product disintegrates with immeasurable rapidity, giving α-rays. Here we have evidence for the first time of penetrating β-rays unaccompanied by γ-rays.

Evidence, however, has been published of a partial separation by chemical methods of thorium-*C* into two numbers responsible for the two kinds of α-radiation.[65] If this is correct, it completely upsets the preceding explanation. Since the evidence is indirect, and all the details of the methods of separation are not fully stated, it may, therefore, be left over, without prejudice, for subsequent consideration, when fuller evidence is forthcoming. The explanation here adopted fits all the known facts provided thorium-*C* is homogeneous. Should it prove separable into distinct products, -C_1 and -C_2, then the dual disintegration must occur earlier, for example, at thorium-*B*. But in this case thorium-C_1 and -C_2 must have the same period. Otherwise, the α-radiation would not decay exponentially. The relative number of α-particles emitted by the successive products shows that a dual disintegration does occur.

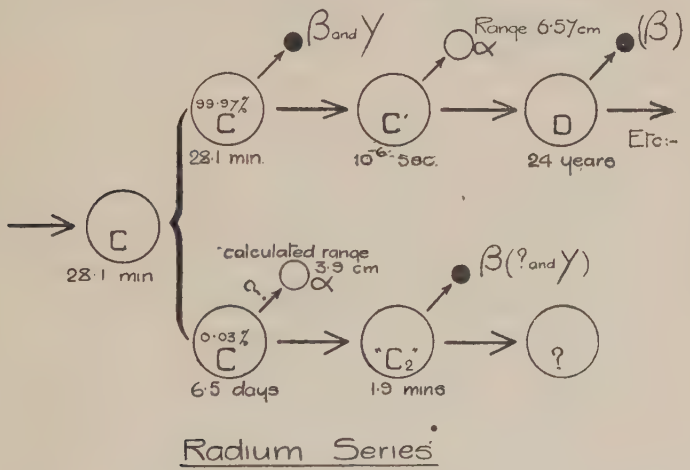
In the whole thorium series six α-particles are expelled per atom of thorium; the calculated atomic weight of the end-product is therefore 232·4 − 23·94 = 208·46, and the nearest known atomic weight is that of bismuth. Two end-products, however, with the same atomic weight in the ratio 35 : 65 must result, if both branches of the series end as the diagram shows.

Radium-C_1 *and* -C_2.—There is not much new experimental evidence

[64] E. Marsden and C. G. Darwin, *loc. cit.* O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1912, **13**, 390; *A.*, ii, 514.

[65] L. Meitner, *Physikal. Zeitsch.*, 1912, **13**, 623; *A.*, ii, 723. Compare also von Hevesy, *Phil. Mag.*, 1912, [vi], **23**, 628; *A.*, ii, 414.

in the case of radium-*C*, but an explanation analogous to that of the thorium dual disintegration may be put forward.[66] In this case the name radium-C_2 has, unfortunately, been applied to a distinct product, of period of average life 1·9 minutes giving β-rays, but not α-rays, separable in very small quantity only by recoil from radium-*C*, that is, from the complex product of period 28·1 minutes, giving α-, β-, and γ-rays. At first the minuteness of the quantity recoiled was attributed to the substance being produced by a β-ray change. But in other β-ray changes, for example, that of radium-*E*, no trace of the product has been observed to recoil. Adopting the view that the relative minuteness of quantity of radium-C_2 is real and not merely apparent, it appears that radium-*C* undergoes a dual disintegration with the ratio λ_1/λ_2 about 3/10,000. That is, some 3 atoms out of every 10,000 of radium-*C* may be supposed to



disintegrate, with expulsion of an α-radiation, of a range which can be calculated to be about 3·9 cm., but which has not yet been detected, producing radium-C_2, which then expels β-rays, and possibly γ-rays also. The remaining 99·97 per cent. of the atoms expel β- and γ-rays, and produce a product of estimated period 10^{-6} second, which on disintegration gives the long range α-rays and produces radium-*D*. In the diagram the hypothetical short-lived product has been termed "*C'*," but it is clear that the whole nomenclature needs to be recast if it should be proved that the thorium and radium series are analogous. These diagrams may prove to be premature. At least, they are interesting.

Evidence in favour of the real relative minuteness of quantity

[66] K. Fajans, *Physikal. Zeitsch.*, 1912, **13**, 699; *A.*, ii, 824.

of radium-C_2 is obtained from the study of the time-β-ray curves of pure radium-*B*, in which the proportion of β-rays contributed by radium-C_2 was too small to be detected.[67]

Incidentally, these experiments confirmed the conclusion of Schmidt, which had been called in question, that radium-*B* emits some penetrating β-radiation. About 1·5 per cent. of the ionisation is due to β-rays [$\mu = 13(\text{cm.})^{-1}\text{Al}$], identical with those of radium-*C*, the remainder being due to the (β)-rays [$\mu = 91(\text{cm.})^{-1}\text{Al}$] commonly ascribed to radium-*B*. No evidence of still softer rays ($\mu = 890$) found by Schmidt was obtained.

Following this up, it was found that radium-*B* also emits γ-rays, and 12·7 per cent. of the ionisation produced by the γ-rays of radium-*B* and -*C* in equilibrium were found to be due to radium-*B*. The absorption-coefficient in lead between 0·3 and 0·6 cm. was 4 $(\text{cm.})^{-1}$, and between 0·97 and 1·72 cm., 6 $(\text{cm.})^{-1}$. These γ-rays are thus of very feeble penetrating power compared with those of radium-*C*, and through 2·3 cm. of lead no γ-rays due to radium-*B* could be detected.

Radioactive Recoil.

A recoiling atom possesses some fifty times the mass and one-fiftieth of the velocity and energy of the α-particle from which it recoils, but, like the α-particle, it appears to be capable of ionising the molecules of the atmosphere in which it is produced.[68] Probably recoil atoms constitute part of the new radiation referred to at the end of the section *δ-Rays*. In the case of radium-*C*, the energy of the α-particles is very great, and the recoiling atoms of radium-*D* possess a "range" one-five hundredth of that of the α-rays of radium-*C*, or about 0·14 mm. of air at atmospheric pressure. At distances within this from a surface of radium-*C*, the recoiling atoms of radium-*D* produce five times as much ionisation as is produced by the α-rays. The fraction of the total ionisation contributed by the recoiling atoms is, however, less than 1 per cent. So far as can yet be seen, the ionising power of the recoil atoms diminishes as the distance traversed in the gas increases, which is the converse of the law holding for α-rays.[69]

Similar experiments with polonium (Ra-*F*), from which the still unidentified and hypothetical end-product of the series must recoil, were unsuccessful until a preparation of the requisite degree of purity was prepared to give a layer thin enough (less than 10$\mu\mu$) to allow the recoil-atoms to escape. Then the ionisation due to the

[67] K. Fajans and W. Makower, *Phil. Mag.*, 1912, [vi], **23**, 292; *A.*, ii, 220.
[68] *Ann. Report*, 1910, 273.
[69] L. Wertenstein, *Le Radium*, 1912, **9**, 6; *A.*, ii, 222.

recoiled atoms became manifest, and the range was estimated as 7 cm. in air at 1 mm. pressure, or rather less than 0·1 mm. at atmospheric pressure. The ratio of the ranges of the recoil-atoms of Ra-*C* and Ra-*F* are nearly the same as the ratio of the ranges of their α-particles.[70] This is the first experimental evidence of the existence of an ultimate product of a disintegration series, as required by the theory.

The absorption of recoil-atoms in passing through a gas has been investigated in the case of radium-*C*. The range of the recoiling atoms of radium-*D* is 10·5 cm. in air at 1 mm. pressure. Hydrogen at 6 mm. pressure is equivalent in every respect to air at 1 mm. In air at 1 mm. the diminution of the number of atoms in a canalised stream of recoil-atoms is unimportant for the first 5 cm., and then increases rapidly to the end of the range. In hydrogen at 6 mm. the diminution is much more abrupt, the lighter atoms of hydrogen probably scattering much less than in the case of air. In each case the ionising power of the recoil-atom diminishes along its path, but the diminution is much more rapid in air than in hydrogen.

The amount of recoil product (actinium-*D* was the product studied) collected on a negatively charged surface is diminished by intense ionisation of the gas. The recoiling atoms behave in this respect like positive ions. Increase in the concentration of the ions in the atmosphere increases the chance of their recombination with ions of opposite sign before they arrive at the electrode.[71]

Influence of Temperature on Radioactive Changes.

The Existence of Chemical Compounds of Short-lived Radio-elements.

A complete explanation has been obtained of the small changes in intensity of the less penetrating types of radiation during the heating and cooling of tubes containing the radium emanation and active deposit.[72]

The effects are not at all due to real changes in the radioactivity, but to alteration of the position of the radiating materials with respect to the measuring instrument by volatilisation and condensation, whereby the mean distance of the source of rays from the instrument and the fraction of the radiation absorbed by the walls of the containing vessel is altered.[73] Thus, if a spherical bulb is employed it can readily be understood that the absorption of the

[70] B. Bianu and L. Wertenstein, *Compt. rend.*, 1912, **155**, 475 ; *A.*, ii, 887.
[71] A. F. Kovarik, *Phil. Mag.*, 1912, [vi], **24**, 722 ; *A.*, ii, 1121.
[72] *Ann. Report*, 1910, 273.
[73] A. S. Russell, *Proc. Roy. Soc.*, 1912, A, **86**, 240 ; *A.*, ii, 416.

radiation in the walls must be less, if the active matter is all in the state of gas, than if it is all deposited uniformly on the walls. In the latter case a greater proportion of the rays reaching an external instrument are tangent to the surface of the bulb, and therefore have paths passing through a maximum thickness of the wall.

Surprising variations occur, however, in the degree of volatility of the various numbers of the "active deposit" groups in different experiments, which were traced to the nature of the atmosphere in which volatilisation took place.[74]

In a vacuum, actinium-*B*, deposited on a surface of platinum or quartz, begins to volatilise at 600°, and volatilisation is nearly complete at 900°. If the deposit is first exposed to various gaseous reagents, such as chlorine or hydrogen iodide, its volatility is increased. Hydrogen chloride, whilst not affecting the volatility, increases the amount of actinium-*B* which can subsequently be dissolved by water, the actinium-*C* being hardly at all soluble under these conditions. In experiments in which a long mica strip was inserted in a tube hotter at one end than the other, a wire coated with actinium-*B* being placed at the hot end, condensation of the volatilised actinium-*B* occurred in air mostly at places heated above 1000°, but in hydrogen the maximum amount was deposited on the surface at a temperature between 615° and 675°.

Similarly with the radium active deposit, in hydrogen volatilisation of all three products, radium-*A*, -*B*, and -*C*, is complete at about 650°, but in an atmosphere containing oxygen no volatilisation of radium-*C* occurs below 1200°, and neither of the three products is volatile below 700°. In hydrogen volatilisation of radium-*C* commences even at 360°. For this substance there is thus a difference of 800° in the volatilisation temperature in hydrogen and oxygen respectively.[75]

These remarkable differences point strongly to the existence of different chemical compounds of these short-lived radio-elements; thus in hydrogen the substance may exist in elementary or metallic form, which is relatively volatile compared with the oxide formed in presence of oxygen. The whole direction in which the subject is moving shows that it is by no means so impossible as appears at first sight to investigate the chemical nature of these ephemeral substances, although they only exist in quantities below the millionth of a milligram.

[74] H. Schrader, *Phil. Mag.*, 1912, [vi], **24**, 125; *A.*, ii, 722.
[75] A. S. Russell, *ibid.*, 134; *A.*, ii, 723.

Electrochemistry of the Radio-elements.

The foregoing remark applies aptly to the electrochemistry of the radio-elements, for in this subject a standing reproach has been that the theory often deals with concentrations entirely beyond the range of verification, as is instanced, for example, by the electrochemical determination of the solubility of almost insoluble substances. Applied to the radio-elements of short-lived period in which a detectable radioactivity is associated with a billionth of a milligram by weight, the electrochemical theory leads to the result that such substances should be deposited from solution in detectable amounts by differences of potential far below the decomposition voltage. In a neutral solution some detectable quantity of a short-lived radio-element should be deposited on any metal, and this theoretical deduction has been verified for all metals, including the noble metals gold and silver, in the case of fifteen separate short-lived radio-elements.[76]

Using concentrations of the order of 10^{-16} g. per c.c., the variation of the ratio in which the *-B* and *-C* members of the series deposited was investigated, as the electrochemical potential of the metal was varied from the case of silver in silver nitrate solution, where the metal is positive to the solution, to that of zinc in zinc sulphate, which is negative. In the first case the *C*-member is deposited almost pure, but as the potential of the metal decreases and changes sign the *B*-member is deposited in increasing quantity until it is in excess of the equilibrium ratio. The *B*- and *C*-members of the three series exhibit identical electrochemical behaviour, and are deposited in equilibrium ratio when the metal is 0·63 volt negative to the solution.

Not the least interesting development was a radioactive method of determining single electrode potentials, for which electrochemical theory cannot be directly tested, from the ratio of the *-B* and *-C* members deposited, and the known variation of this ratio with the P.D. actinium-*B* and *-C* furnishes the quickest, and thorium-*B* and *-C* the most accurate indicator for this purpose, radium-*B* and *-C* being unsuitable. The ratio is deduced from the α-ray decay curve of the deposit; thus for a copper electrode immersed in pure water for one minute the potential difference between metal and solution was $-0{\cdot}7$V., and for an immersion of 0·2 second, -2V. With longer immersion the normal electrochemical potential of copper is approached. These are beautiful illustrations of how deductions from the theory of solution pressure in cases where the ionic concentration of the metal approaches zero may be tested.[77]

[76] G. von Hevesy, *Phil. Mag.*, 1912, [vi], **23**, 628; *A.*, ii, 414.

[77] G. von Hevesy, *Physikal. Zeitsch.*, 1912, **13**, 715.

Von Lerch's general method of separating the -*C* member from the -*B* member in a pure state by deposition on nickel depends partly on the abnormal negative potential of the nickel electrode, which is connected with its passivity, and on the use of an acid solution in which the -*B* member deposited is preferentially dissolved. In the three series radium-*C* is the easiest and thorium-*C* is the most difficult to separate from the -*B* member in the pure state, whereas from the molecular equilibrium ratio in the three series, actinium-*C* should be the most difficult of the three. This anomaly would be explained if thorium-*C* really consisted of two separate substances, C_1 and C_2, of which only the one, C_1, giving the shorter range α-rays and present in less proportion, is analogous to the other *C*-members. The point is, however, too crucial to be settled by such indirect evidence.

Ionium.

Homogeneity of Chemical Elements.

The results of experiments that have been in progress over the past seven years on the growth of radium from large quantities of uranium in solution purified in various ways have recently been collected and discussed.[78] A minute growth, which, expressed in units of 10^{-12} gram of radium per kilogram of uranium per year, varied from 12·4 for the first to 2·0 in the last quantities purified, was observed in all the uranium preparations, but, so far as can be seen, it is proportional to the time and is due to minute traces of ionium originally present. No indication of an increased rate of growth of radium, such as must occur if ionium in appreciable quantity was forming during the time of observation, has yet been observed. It may be calculated that, if ionium is the only long-lived intermediate substance in the series between uranium and radium, its period of average life must be at least 100,000 years, which is forty times longer than that of radium, and the quantity in uranium minerals must be at least 12·3 grams per 1000 kilos. of uranium. The total quantity of ionium and thorium together in Joachimsthal pitchblende is such that the maximum estimate for the period of ionium can hardly be greater than a million years, and has recently been estimated by this method on certain assumptions to be not more than 250,000 to 300,000 years.[79] These estimates are supported by the failure to detect the growth of ionium from uranium-*X*, the product of which remains experimentally unknown.[80] They all involve the assumption that no unknown

[78] F. Soddy, Royal Institution Lecture, March 15th, 1912; *Nature*, 1912, **89**, 203.

[79] St. Meyer and V. F. Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, II.; *A.*, ii, 603.

[80] *Ann. Report*, 1909, 262.

intermediate substances of long life intervene. On the other hand, the period of 200,000 years, estimated from the range of the ionium α-particle (p. 294), does not involve this assumption, and is in good agreement with the other estimates.

The question, whether unknown long-lived intermediate members of the series still remain to be discovered, has, however, been raised in an acute form by the failure to detect, in the arc spectra of the strongest ionium-thorium preparations, a single new line due to ionium.[81] Such preparations, from the intensity of their α-radiations, must contain more than 10 per cent. of ionium if the period is 100,000 years, and, it is reasonably certain, should show at least some of the lines of the ionium spectrum. The strongest line of the radium spectrum can be detected in a barium preparation containing only a few parts of radium in a million. Not a single unknown line has, however, been observed. In one investigation in addition to the thorium spectrum, only five of the stronger lines of scandium were observed. In the other investigation, cerium, scandium, yttrium, and some of the rare earths were detected. It may be mentioned that the proportion of ionium and thorium in a preparation of the oxides is not affected by heating in the electric arc.

An interesting line of thought may now be pursued. The complexity of "uranium" and the view that it consists of two non-separable elements, uranium-*I* and uranium-*II*, differing in atomic weight by four units, raises the question whether uranium-*X*, the product of "uranium," is the product of uranium-*I* or of uranium-*II*. There is really no experimental evidence whatever capable, at present, of deciding between the two alternative schemes:

$$\text{Ur-}I \xrightarrow{\alpha} \text{Ur-}II \xrightarrow{\alpha} \text{Ur-}X \xrightarrow{\beta} \text{Io} \xrightarrow{\alpha} \text{etc.}$$

$$\text{Ur-}I \xrightarrow{\alpha} \text{Ur-}X \xrightarrow{\beta} \text{Ur-}II \xrightarrow{\alpha} \text{Io} \xrightarrow{\alpha} \text{etc.}$$

Hitherto, the first has always been assumed, but the second is much the more probable. For the first scheme is an exception to the rule that the expulsion of an α-particle reduces the valency by two units, the step being always from the family of even valency into the next, the family of odd valency being always missed.[82] The second scheme not only conforms to this rule, but exhibits also the well-marked alternation, shown in other cases, in which the next change, in which an α-particle is not expelled, causes

[81] F. Exner and E. Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, IIa, 1075; A. S. Russell and R. Rossi, *Proc. Roy. Soc.*, 1912, A, **87**, 478.

[82] Soddy, "Chemistry of the Radio-Elements," p. 30.

the atom to revert to its original group. This is shown by the following comparison of the uranium and thorium series:

$$\underset{\text{IV.}}{\text{Th}} \xrightarrow{\alpha} \underset{\text{II.}}{\text{MsTh}} \xrightarrow{\beta} \underset{\text{IV.}}{\text{RaTh}} \xrightarrow{\alpha} \text{Th-}X \xrightarrow{\alpha} \underset{\text{O.}}{\text{Em}} \xrightarrow{\alpha} \text{etc.}$$

$$\underset{\text{VI.}}{\text{Ur-}I} \xrightarrow{\alpha} \underset{\text{IV.}}{\text{Ur-}X} \xrightarrow{\beta} \underset{\text{VI.}}{\text{Ur-}II} \xrightarrow{\alpha} \underset{\text{IV.}}{\text{Io}} \xrightarrow{\alpha} \underset{\text{II.}}{\text{Ra}} \xrightarrow{\alpha} \underset{\text{O.}}{\text{Em}} \xrightarrow{\alpha} \text{etc.}$$

The figures refer to the families in the Periodic Tables to which the elements belong. All the members in *both* series designated by the same numeral (O, II, IV, and VI) are chemically identical, so far as is known.[83]

Obviously, if uranium-*II*, and not ionium, is the product of uranium-*X*, the experiments above referred to with the latter substance do not furnish a minimum estimate of the period of ionium, as hitherto supposed, but of that of uranium-*II*. The reasoning, however, as regards the absence of growth of radium from uranium remains unmodified, for the two uraniums necessarily always exist together in equilibrium proportion.

The simplest, if somewhat heterodox, view to take is that ionium is a long-period element, and that its spectrum, as well as its whole chemical behaviour, is identical with that of thorium. It is clear that the conception of chemical elements as necessarily homogeneous is undermined, and that different elements with different atomic weights are chemically identical, not as an exception, but as a consequence of the way in which the known disintegration series have been shown to run their course. In non-radioactive matter this heterogeneity cannot be distinguished. Not so in the case of matter actually in the process of evolution.

Chemical Action of the Rays of Radium.

In an investigation of the ozonisation of oxygen by α-rays the number of ozone molecules formed was found to be of the same order as the number of pairs of ions produced. The ratio between these two quantities varied capriciously, and was in no case greater than 1:2, frequently being less. The results were consistent with the view that the ozone results in a reaction between the oxygen ions and molecules, but that unknown causes produced a loss of the ozone formed, which varied according to the conditions.[84]

The statement that radium emanation exerts a decomposing effect

[83] Compare A. Fleck, Paper read before Section B, British Association Meeting, Dundee, 1911; *Chem. News*, 1912, **106**, 128. The full results, obtained in the author's laboratory, are in course of publication. Some of them bear on the subjects discussed in this section.

[84] S. C. Lind, *Monatsh.*, 1912, **33**, 295; *Le Radium*, 1912, **9**, 104; *A.*, ii, 513.

on sodium urate, converting it into easily soluble substances, has been submitted to an exhaustive examination, and disproved.[85]

Many of the reactions accelerated or brought about by light or ultraviolet light have been examined under the influence of the penetrating rays of radium. The effects produced by the latter are often very small by comparison. No increase in the rate of esterification of benzoic acid by alcoholic solution of hydrogen chloride, no effect on *p*-benzoquinone in alcoholic or ethereal solution, and no action on normal aqueous solutions of oxalic acid at 25°, could be observed, although very powerful radium preparations and long exposures were employed. The formation of the acid from *o*-nitrobenzaldehyde in alcoholic or benzene solutions was accelerated by radium rays, although to an extent between 10,000 and 20,000 times smaller than is produced by ultraviolet light from a quartz mercury lamp at 8 cm. distance. As with ultraviolet light, the rays of radium effect a marked increase in the rate of inversion of unsterilised neutral sucrose solutions, but they act oppositely to ultraviolet light in favouring the growth of mould in sugar solutions.[86]

The liberation of iodine from solution of alkali iodides by the penetrating rays of radium is notably increased by presence of free acid, as though the alkali produced had a retarding action, and, like most photochemical actions, is not much influenced by increasing the temperature. Potassium iodide is far more sensitive to this reaction than sodium iodide.[87] Similarly, at least in acid solution, bromine is liberated from solutions of potassium bromide, but the action is less marked than with the iodide. Acidified potassium chloride solutions are unaffected.

The velocity of decomposition of hydrogen peroxide is greatest in acid and least in alkaline solutions, and no difference was observed when paraffined glass vessels were employed. Ferric sulphate, especially in the presence of sucrose, is reduced by penetrating radium rays as it is by light.[88]

Biochemical Effects of Radioactivity.

Three important communications deal with the differences brought about by radioactive agencies in the development of plants, the sprouting of buds of different woods, and the growth of seeds. In

[85] E. v. Knaffl-Lenz and W. Wiechowski, *Zeitsch. physiol. Chem.*, 1912, **77**, 393; *A.*, ii, 522.

[86] A. Kailan, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, IIa, 1329; *A.*, 1913, ii, 8.

[87] A. Kailan, *Monatsh.*, 1912, **33**, 71; *A.*, ii, 522.

[88] *Ibid.*, 1329; *A.*, 1913, ii, 7.

the first,[89] watering with radioactive water from Joachimsthal, of 300 to 2000 Mache units strength, some seven varieties of plants (*Triticum vulgare, Hordeum disticum, Vicia faba, Pisium sativum, Lupinus angustifolias, Trifolium pratense,* and *Pisium arvense*) produced after a week strikingly favourable effects on the growth. The roots and stalks increased several times in length, and the weight of dried matter in the stalks was from three to five times greater than in the case of plants watered with inactive water of the same chemical composition. On the other hand, various bacteria (*B. mycoides, fluorescens liquefaciens, pyocyaneum,* and *filefaciens*) were harmfully affected by the active water, whereas *Azobacter chroococcum,* the nitrogen assimilating bacterium, was not so much affected.

In the second paper,[90] it was found that the winter buds of various woods such as *Syringa vulgaris,* when exposed for one or two days to the rays of strong radium preparations, or, better, under a bell-jar in an atmosphere containing a few millicuries of emanation, sprouted when subsequently cultivated in the hot-house in the light, whereas other buds not treated did not sprout at all or only much later. Too little exposure to the rays is without effect, and too much exposure is harmful or fatal to the plant. At other periods of the year no result is produced, and the effect is quite distinct from that produced on the growing plant.

Lastly,[91] the influence of the radium β-rays of different penetrating power on the development of small seeds, under 0·7 mm. diameter, has been studied. It was found that the growth was hindered by irradiation with β-rays from 8 milligrams of radium at a distance of 1 cm., independently of the chemical constitution of the seed (starch and fat content), which varied widely, and was greater for the less penetrating than for the more penetrating rays, when rays of equal ionising power were compared. The retardation of the growth is not noticeable for short exposures (five hours). After the fifth hour for the first day, the retardation increases rapidly with the exposure, and then increases less rapidly for longer exposures up to three or four days. It is possible that very short exposures have a favourable influence on *Sinapis nigra* and *Panicum germanicum.*

Various.

It is convenient to collect together a number of observations of special rather than general interest.

Emanations.—The actinium emanation is dissolved by various

[89] J. Stoklasa, *Compt. rend.*, 1912, **155**, 1096.

[90] Hans Molisch, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, I, 121.

[91] E. D. Congdon, *ibid.*, 1911, **120**, II*a*, 1327.

liquids and by charcoal very much as in the case of the other emanations, but is rather more soluble. The coefficient of solubility in water is 2, that of the thorium emanation being 1, and of the radium emanation, 0·33.[92] There is no difficulty in detecting the presence of actinium in a uranium mineral by means of its emanation, provided small containing vessels and rapid currents of air are employed.[93] The diffusion of the actinium emanation has been further studied, and compared with that of the thorium emanation. All that can be said is that the molecular weights of these two emanations must be nearly equal.[94]

Active Deposits.—Two researches have been made on the distribution of the active deposit of radium under various conditions between the positive and negative electrodes.[95] The proportion of the active deposit finding its way to the cathode varies much in the same way as the ratio of the ionisation current in the gas to the saturation current under the same conditions. To account for the deposition of the active products on the anode, it is suggested that the positive charge on the atoms of radium-*A* at formation is neutralised, and in the case of some 2 per cent. reversed by combination with negative ions in the gas.

Negative Results.—No radioactivity is produced in such metals as bismuth, antimony, and iron by the application of a high frequency alternating magnetic field,[96] nor in various chemical reactions, such as the decomposition of hydroferrocyanic acid by heat, the reduction of potassium dichromate by heating with oxalic acid and of potassium permanganate by heating alone or with reducing agents.[97] The radioactivity of rubidium and potassium salts is unaffected by exposure to light. No α-rays could be detected from these compounds, and the thermal effect of their radioactivity is too small to be observed.[98]

As regards the existence of radio-uranium, no evidence except negative evidence is forthcoming.[99]

Uranium-*Y* also must be classed with the substances the existence of which is in need of confirmation.

[92] G. von Hevesy, *Physikal. Zeitsch.*, 1911, **12**, 1214; *A.*, ii, 117.

[93] *Idem.*, *ibid.*, 1213; *A.*, ii, 116.

[94] Miss M. S. Leslie, *Phil. Mag.*, 1912, [vi], **24**, 637; *A.*, ii, 1032; J. C. McLennan, *ibid.*, 370; *A.*, ii, 889.

[95] E. M. Wellisch and H. L. Bronson, *ibid.*, **23**, 714; *A.*, ii, 521; G. Eckmann, *Jahrb. Radioaktiv. Elektronik*, 1912, **9**, 157; *A.*, ii, 620.

[96] J. H. Vincent and A. Bursill, *Proc. Physical Soc.*, 1912, **24**, 71; *A.*, ii, 417.

[97] W. A. D. Rudge, *Proc. Camb. Phil. Soc.*, 1912, **16**, 465; *A.*, ii, 519.

[98] E. H. Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 22; *A.*, ii, 724.

[99] H. Sirk, *Monatsh.*, 1912, **33**, 289; *A.*, ii, 519.

Radioactivity of the Earth and Atmosphere.

The fusion method of estimating radium in rocks[1] has been used in a systematic revision, characterised by the feature that, instead of samples of individual rocks, mixed samples composed of a large number of specimens of different rocks of the same class were dealt with. Only undifferentiated materials are included. These results establish a substantial difference between the radium content of igneous and sedimentary rocks, which had been questioned by another investigator. In terms of units of 10^{-12} gram of radium per gram of rock, the means for igneous rocks, divided into three classes, are: (1) acid, 3·01; (2) intermediate, 2·57; (3) basic, 1·28, whilst for sedimentary rocks the mean is 1·4, excluding the calcareous sediments for which the mean is 0·8.[2]

The mean of the previous results obtained by the solution method, excluding Joly's results, which are higher, are distinctly lower than these new determinations, being, for the three classes of igneous rocks, 2·17, 1·28, and 0·58 respectively.

If 2 is taken as a mean quantity of radium for all the rocks of the crust, and 2×10^{-5} gram of thorium per gram of rock is included, the heat generated is 25×10^{-14} calorie per gram per second, and a depth of 17 kilometres would supply all the heat reaching the surface of the earth from the interior. The increase of temperature at the base of this 17 km. layer would be only 246° under equilibrium conditions. If the internal heat is to be entirely attributed to radioactive changes and a state of thermal equilibrium is postulated, it is necessary to suppose that the radioactive layers are less rich than the average surface materials and extend to a greater depth than 17 km. For as Joly has deduced in a general manner, a given quantity of the radio-elements will generate at the base of the layer a higher equilibrium temperature the more they are diluted with inactive material, and the greater the depth of the layer in consequence.

So far as investigations have proceeded, there does not appear to be any systematic variation of the radium content of rocks with the depth from which they are taken, and rocks from a great variety of localities exhibit results closely in accord with the general mean.[3]

A number of investigations deal with the emanation content of

[1] *Ann. Report*, 1911, 293; compare E. Ebler, *Zeitsch. Elektrochem.*, 1912, **18**, 532; *A.*, ii, 723.

[2] J. Joly, *Phil. Mag.*, 1912, [vi]. **24**, 694; *A.*, ii, 1032; A. L. Fletcher, *ibid.*, **23**, 279; *A.*, ii, 224.

[3] E. H. Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 1063; *A.*, ii, 525.

air drawn from the underground soil at various depths, and the escape of emanation into the atmosphere. It is clear that the quantity of emanation in the atmosphere is continuously maintained by the amount escaping from the soil. The air drawn from even a metre or less below the surface of the ground is several thousand times richer in radium emanation than the atmosphere, a mean value in one series being 2×10^{-10} curie per litre. The supply of emanation is, as is to be expected, not exhausted by the continuous withdrawal of the air. Even so, it has been estimated that only about 1/70th of the emanation generated by the radium in the soil escapes into the underground air, and this also is what is to be expected from the known small proportion of emanation which ordinarily escapes from solid substances containing radium. For the purposes of comparison, it may be stated that the 5000 litres of gas escaping daily from the Bath springs are estimated to contain $1{\cdot}7 \times 10^{-4}$ curie of emanation. Volume for volume, this is about 200 times richer in emanation than the underground air, for example, in the neighbourhood of Cambridge and Dublin. The escape of emanation into the atmosphere, and the consequent impoverishment of the underground air in emanation, is facilitated by a strong wind and hindered by frost and rain, but the fluctuations of the barometer, apart from accompanying storms and rain, is without direct influence.[4]

In a voyage from Valparaiso to the East Indies, the emanation content of the sea water was found to change to an extraordinary content with the locality, increasing with the specific gravity and temperature of the water. The active deposit in the atmosphere was probably not derived from the emanation in the ocean, but from emanation carried from the land by winds.[5]

The question of the origin of the earth's penetrating radiation, whether it comes from the earth or the atmosphere, is attracting attention. Most investigators believe that in the free air the penetrating rays come from the earth, although very near the surface the effect of a superficial active deposit from the atmosphere can be detected.[6] It is noteworthy, however, that in two recent balloon voyages, one at night and the other during the day, in which a specially constructed thick-walled Wulf electrometer was carried, at heights for the most part about 200 metres from the earth, although the maximum height was about 1000 metres, no definite diminution of the effect due to penetrating radiation was

[4] L. B. Smyth, *Phil. Mag.*, 1912, [vi], **24**, 632 ; *A.*, ii, 1031 ; J. Satterly, *Proc. Camb. Phil. Soc.*, 1911, **16**, 336, 356, 514 ; *A.*, ii, 117, 118, 522.

[5] W. Knoche, *Physikal. Zeitsch.*, 1912, **13**, 112, 152 ; *A.*, ii, 223.

[6] A. Gockel, *Jahrb. Radioaktiv. Elektronik*, 1912, **9**, 1 ; *A.*, ii, 416 ; W. Strong, *Terrestial Magnetism*, 1912, **17**, 49.

observed.[7] At 200 metres from the earth's surface, reckoned as a uniform source of γ-rays of radium of infinite extent, the absorption of the air should reduce the intensity of radiation as much as a layer of 1·83 cm. of mercury, and this should, of course, be very noticeable.[8] Probably, however, the instrument was not sufficiently good to use for the purpose. As is recognised by everyone who has attempted to reduce the natural leak of an electroscope to its absolute minimum, the effect of the radioactivity of the walls is the chief contributor to the natural leak unless very special means, which it is not wise to leave to the instrument maker, are adopted. This seems to have been the case in the present instance. The influence of the varying amount of ballast carried by the balloon has also been alluded to.[9]

The spectrum of *Nova Geminorum* (1912), which shows a general resemblance to that of the solar chromosphere, contains lines which have been ascribed to radium and its emanation. This has led to the spectrum of the solar chromosphere during the eclipses of 1898, 1900, 1901, and 1905 being re-examined, with the result that agreement has been found between some of the lines and those of the radium spectrum. The evidence, however, is conflicting, and the fact that radium is the source of these lines appears extremely difficult to believe.[10]

FREDERICK SODDY.

[7] V. F. Hess, *Sitzungsber K. Akad. Wiss. Wien*, 1911, **120**, II*a*, 1575.

[8] An exact expression for the absorption is given by L. V. King, *Phil. Mag.*, 1912, [vi], **23**, 242.

[9] L. V. King, *loc. cit.*

[10] *Astronom. Nachr.*, 4582, 4589, 4600.

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ERRATA.

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Page		Line.	
21		12–13	The names "Rhombic sulphur, S_1" and "Prismatic sulphur, S_2" should be interchanged. This error, which originated in the German paper (*Zeitsch. physikal. Chem.*, 1911, **77**, 661) and was reproduced in the abstract (1911, ii, 977) is now corrected on the authority of a personal letter from the author. T. M. L.
164	Footnote	50 Line	*for* "C. Rawson" *read* "S. G. Rawson."
310		3*	„ "C. Rawson" „ "S. G. Rawson."

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